TAMPEREEN TEKNILLINEN YLIOPISTO

ANU HONKALA

LIGHT AND EFFICIENT WEAR RESISTANT HYBRID MATERIALS

Master of Science Thesis

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ABSTRACT

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The advantages of the adhesive bonding are widely understood and there is an increasing demand for the adhesives in the new kind of industrial applications. The advanced adhesive technologies are increasingly replacing the traditional fasteners and competing with the other bonding techniques as they can lighten the structures, extend the service life, improve the product performance and/or reduce the amount of the manufacturing steps. Hybrid materials are one of the rapidly growing application areas of the adhesive bonding.

Hybrid materials combine the properties of two or more different materials to create new functionalities for the existing products or to develop totally new applications. Joints or interfaces are in the heart of the hybrid material formation since the creation of the hybrid component involves joining of various materials or components. Bonding between the materials is critical to the mechanical integrity of the overall hybrid structure.

The objective of this thesis was to find out whether the planned hybrid structure would be durable enough to be used as a wear part. The studied structure contained thin layers of steel and polymer, of which the polymer component was outlined as the research subject of the study.

In the literature survey part the theory of the hybrid- and composite materials, adhesive bonding, wear and the wear and failure mechanisms of the polymers were studied. The related test methods, environmental issues and manufacturing processes were also reviewed. In the practical part the feasibility and usability related to durability of the polymer part of the planned hybrid structure were studied. The test procedures contained the lap shear tests to obtain information about the most important durability related mechanical properties of the structure. The polymer materials for the tests were selected based on the operating environment requirements.

Different results were achieved depending on the test variable combination. The results also showed that a sufficiently durable polymer-steel hybrid structure may well be achieved. Yet it is important to establish better adhesion between the polymer and the steel parts. In addition the joint needs to be more moisture resistant.

TIIVISTELMÄ

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Adheesion hyödyt liittämisessä ovat laajalti ymmärretty, joten sen käyttäminen myös teollisissa sovelluksissa on alati kasvamassa. Edistykselliset liimateknologiat ovat enenevässä määrin syrjäyttäneet perinteisiä kiinnittimiä ja ne kilpailevat myös muita liittämistekniikoita vastaan, sillä niiden avulla on mahdollista esimerkiksi keventää rakenteita, laajentaa käyttöikää, parantaa suorituskykyä ja/tai vähentää tuotantovaiheiden määrää. Hybridimateriaalit ovat eräs nopeasti kasvavista adheesioon perustuvista sovellusalueista.

Hybridimateriaaleissa on yhdistetty kahta tai useampaa materiaalia niin, että esimerkiksi nykyisiin tuotteisiin on saatu tuotua uusia toiminnallisuuksia tai luotua kokonaan uusia käyttösovelluksia. Koska hybridimateriaali syntyy yhdistämällä erilaisia materiaaleja, on liittäminen keskeistä sen valmistamisessa. Mekaanisesti yhtenevän rakenteen saavuttamiseksi on materiaalisidoksilla erittäin suuri merkitys.

Tämän opinnäytteen tavoitteena oli selvittää saadaanko suunnitellun hybridirakenteen avulla luotua riittävän kestävää kulutusosaa. Tutkittava rakenne sisälsi ohuita teräs- ja polymeerikerroksia, polymeeriosan ominaisuuksien ollessa tarkemman tutkimuksen kohteena.

Työn teoreettisessa osassa keskityttiin hybridi- ja komposiittimateriaaleihin, adheesioon, kulumiseen yleisesti ja polymeerimateriaalien vikaantumis- ja kulumismekanismeihin. Lisäksi tarkasteltiin aihealueeseen liittyviä testausmenetelmiä, ympäristönäkökohtia ja valmistusteknologioita. Kokeellisessa osassa tutkittiin hybridirakenteen polymeeriosan soveltuvuutta ja käytettävyyttä kohteeseen. Hybridirakenteen kestävyyteen liittyviä ominaisuuksia testattiin muun muassa leikkauslujuuskokein. Testattavien polymeerimateriaalien valinta perustui lopullisen käyttöympäristön vaatimuksiin.

Testeissä saatiin erilaisia tuloksia riippuen testimuuttujayhdistelmistä. Tuloksien perusteella riittävän kestävä hybridirakenne voi hyvinkin olla saavutettavissa. Olisi kuitenkin tärkeää saada muodostettua parempi adheesio polymeerin ja teräksen välille. Liitoksen tulisi myös olla kestävämpi kosteuden vaikutuksia vastaan.

PREFACE

This Master of Science Thesis was carried out at Tampere University of Technology at the Department of Materials Science during the spring and summer 2012. It was funded by the research project under the Light and Efficient Solutions Program (LIGHT) of Finnish Metals and Engineering Competence Cluster Ltd (FIMECC).

During this thesis work I got to explore deeper in the world of the polymers in a form of the adhesives and adhesion. My knowledge of the polymer materials and chemistry expanded a lot. Also wear related issues came more familiar.

First I wish to thank my supervisor professor Jyrki Vuorinen for the inspiring work opportunity and the guidance and support I received during this work. I also thank Olli Orell for his guidance, advices and support. Also Markus Kakkonen receives thanks for his advices and help, Matti Hautala for the interesting discussions and making of the specimen jigs and Kati Mökkönen for the help with testing. I would also like to thank Marke Kallio, Riina Lahtomäki and Vesa Villman for the discussions and tips during the thesis work.

Last but not least, I want to express thanks to my family and friends for their encouragement. Especially my husband Janne is appreciated for his support and understanding during all these years I have used for this degree. And to Kia and Noa: thank you for your patience, now it is your turn.

Tampere 17.10.2012

Anu Honkala

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ABBREVIATIONS

ASTM	American Society for Testing Materials
CTE	Coefficient of thermal expansion
DCB	Double cantilever beam
DIN	Deutsche Industrienorm
DMTA	Dynamic mechanical thermal analysis
EU	European Union
FIMECC	Finnish Metals and Engineering Competence Cluster Ltd
ISO	International Organisation for Standardisation
LIGHT	Light and Efficient Solutions Program
MDI	Methyl di-isocyanate
RH	Relative humidity
RIM	Reaction injection moulding
RRIM	Reinforced reaction injection moulding
RTM	Resin transfer moulding
SRIM	Structural reaction injection moulding
TDI	Toluene di-isocyanate
T_g	Glass transition temperature
T_m	Melting temperature

TERMS AND DEFINITIONS

Adherend	Substance to which an adhesive bond is being made, sometimes referred to as a substrate
Adhesion	Attraction between two connected substances which requires work to be done to separate them
Adhesive	Substance that joins components together by forming an interfacial bond between them
Cohesive force	Attractive force between the molecules within a material
Curing	During curing the thermosetting resin transforms into a hardened rigid state due to the crosslinking
Dispersant	Something that disperses
Interphase	Transition region between two bulk materials (for example between the polymer and reinforcement)
Load cell	Transducer which converts a value of force into a proportional measurement signal
Pot life	Period of time, working life, in which a multipart adhesive can be used after mixing
Pre-treatment	Preparation of an adherend surface to increase the adhesive bonding characteristics
Primer	Special coating designed to improve adhesion between adhesive and adherend and to prevent oxidation
Pyrolysis	Thermochemical decomposition of organic material at elevated temperatures without the participation of oxygen
Resin	Natural or synthetic compound which begins in paste or liquid state and hardens with treatment
Solvent	Substance that dissolves another to form a solution
Strain	Deformation that is caused by the stress
Stress	Intensity of loading at any point
Spherulite	Spherical semi-crystalline region inside non-branched linear polymer
Thixotropy	Property exhibited by certain gels of becoming liquid when stirred or shaken
Tribology	Tribology is about friction, wear and lubrication
Wetting	Extent to which a liquid will come into contact with a surface to which it is applied

1 INTRODUCTION

Hybrid materials are one of the rapidly growing application areas of the adhesive bonding. The advanced adhesive technologies are increasingly replacing the traditional fasteners and competing with the other bonding techniques as they can lighten the structures, extend the service life, improve the product performance and/or reduce the amount of the manufacturing steps. Hybrid materials combine the properties of two or more different materials to create new functionalities for the existing products or to develop totally new applications. Joining is at heart of the hybrid material formation since the creation of the hybrid component involves joining of various materials or components.

In this thesis the subjects of experiments were on the polymer-metal hybrid materials. The studied structure contained thin layers of steel and polymer, of which the polymer part was outlined as a research subject. The scope of this study was to found out whether the planned polymer-hybrid component would be durable enough to be used as a wear part of a machine.

In the literature survey part's chapters 2 and 3 the theory of the hybrid materials, adhesive bonding, wear and the wear and failure mechanisms of the polymers are discussed. In chapter 4 the background requirements for the hybrid component are introduced. The applicable manufacturing processes are presented in chapter 5. The environment and safety related issues are discussed in chapter 6. In chapter 7 the material selection process, requirements for the polymer material and the received test components are introduced. Also general material chemistry and the properties of the chosen materials and the surface treatment related issues are explained.

In the practical part the feasibility and usability related to durability of the planned hybrid structure were studied. The different test methods related to the thesis field and the test methods used are presented in chapter 8. The results are discussed in chapter 9 and the conclusions are found in chapter 10.

2 THEORY OF HYBRID MATERIALS

High specific strength and modulus, cost-effective fabrication and multifunctional characteristics have made the high-performance polymers the materials of choice for the engineering, defence, electronics and medical applications. It is possible to alter the stress-strain behaviour of a polymer (for example by adding plasticisers or fillers). The mechanical strength or the impact toughness may also be increased by increasing the polymer chain length or by crosslinking the chains. Toughening rigid polymers with a second rigid phase has been a great success in the plastics industry. The ultimate objective of hybridization is to create and combine an engineered proportion of the material components for a range of applications. Mechanical behaviour sets the basis for the acceptable material's performance. [1]

So the hybrid materials aim at utilising a full advantage of two or more material classes by combining them in a single component/structure. The object is to gain such a combination that the resulting hybrid material offers performance which could not be achieved by either of the two or more constituents independently. For example a component made from the polymer-steel hybrid material may replace a cast steel component. In general the adhesive bonding is utilised in order to form the polymer metal hybrid materials. Furthermore when compared to the mechanically bonded materials the adhesively bonded materials offer advantages such as higher stiffness and better fatigue performance, which are yet more reasons why the number of the adhesive applications in various industries is steadily growing. Typical examples of the useful applications of the adhesive bonding technology are in the construction of aircrafts, rail vehicles and automobiles. [2, 3]

2.1 Definition of composite and hybrid material

Recently, the word hybrid has become a word used more in materials science and engineering. While the term hybrid materials have been used to express materials that have been mixed/joined with different materials, the materials consisting of different materials are conventionally called composites. In many cases, when the word hybrid is

used, the term is not defined, and the difference between the hybrid material and composite is not clear. [4] In general, the hybrid materials are combinations of two or more materials in attempt to get the best of each. The components of the material are not dissolved or completely blended into each other. [3]

A traditional composite material consists of a continuous phase that is called matrix and a reinforcing phase. The commonly used reinforcements with the polymer matrix are for example glass, carbon and aramid fibres. Reinforcement form can be for example particulate, whisker, flake or fibre. The architecture of the fibres may be continuous (such as cloth, long fibres or roving) or discontinuous (such as short fibre or chopped roving). Matrix can be based on the polymeric, metallic or ceramic material. Both thermoplastic and thermosetting polymers are used as a matrix material though the thermosets are more common. [5, 6] With the fibre reinforced composites the matrix transmits load to the fibres, which are the primary components bearing load. In addition the matrix protects the fibres from the mechanical and environmental damage and maintains the fibre orientation [6]. Bringing the favourable orientations and the different types of fibre together may lead to further improvements, to so called synergistic effects [5]. The addition of the fibres tends to improve properties such as stiffness, impact resistance or thermal conductivity [7]. It should also be noted that not all fillers are of benefit to the performance of the composites [5].

With the hybrid materials it is possible to expect very interesting characteristics that are not found in the combined materials independently. For example, there may exist features such as being flexible like some plastics but still possess excellent mechanical strength and thermal stability [8] or a superior performance and/or the new functions in comparison with their component monolithic counterparts. [4] As an example the laminar metal-plastic-hybrids are made by an adhesive bonding process where the polymer acts as a binding agent. These hybrids which are composed of thin layers of metal and polymer (or polymer composite) materials may have for example lower specific weight and better impact resistance.

One group, which has received a great deal of attention from the many different fields, is the inorganic/organic hybrids. Within classical definition of hybrids such as composites, sandwiches or foams this is a newer category of materials, possessing particular chemical bonds, which are different from the characteristic chemical bond, between the inorganic and organic materials. In the inorganic/organic hybrids this specific chemical bond produces excellent properties in the macroscopic scale. These

materials are based on the interactions between the different molecules. [4] The inorganic/organic hybrid materials are increasingly important due to their extraordinary properties, which arise from the synergism between the properties of the components. These materials have gained much interest due to the remarkable change in the mechanical, thermal, electrical and magnetic properties compared to the pure organic polymers. [9]

The functionally gradient materials can be of technical interests when the components have to have different properties at different locations of their cross-section. For example hardness and abrasive wear resistance may exist on the outside, toughness and damage tolerance on the inside and there are no sudden property jumps in between. [5]

2.2 Why to use hybrid materials

The polymeric materials are used in various designs because of their advantageous material properties such as low weight, low cost and good processibility [6]. There are two main characteristics which make the polymers and the reinforced polymers attractive compared to the conventional metallic materials, those are relatively low density value and controllable tailoring capability to provide the required properties such as strength and/or stiffness [10].

The hybrid materials can occupy spaces on the material property charts not occupied by the monolithic materials. The design requirements can be in a direct conflict so that no single material is able to provide the property profile needed. In such occasion the hybrid material may allow an innovative design solution and improvement in performance, exploiting the individual properties of the component materials. [3]

There are various background points why the hybrid materials have attracted the attention. For example it has become possible to carry out high precision molecular design and structural control, even at the nanometre levels, as the research instruments have developed and are capable of characterization of nanometre or even smaller sizes. In consequence interesting and unique phenomena have been found. So instead of developing totally new materials by controlling the conventional materials in finer scale it is possible to obtain the extraordinary improvements in the material characteristics. [8] There are new developments under way to explore the new fields of application for these materials. And their properties can be tailored for the more extreme conditions. [5]

2.3 Adhesive bonding and joining

The use of adhesion for the practical purposes goes back a long way, over several thousands of years. The first adhesive factories started on the 17th century and the synthetic resins development started on the early 20th century. At the same time the advantages of the adhesive bonding compared to the other joining and fastening methods were already widely understood.

The performance of the bonded joints is improving and the expectations of bonding have become higher, thus the requirements for the high strength adhesives have become greater as well. When the bonding process and application control are appropriate the adhesive products are able to show very high bond strengths. [11]

Joining is at the heart of the hybrid formation since the creation of these components involves joining of the various materials or components. Bonding between the components is critical to the mechanical integrity of the overall structure. Joining may be achieved for example by sintering, welding or adhesion. Sintering is one of the forms of the diffusive adhesion. A welded joint is a joint made by melting the parts of the components involved in the joint at their interface and their subsequent solidification upon cooling. The welded joint is based on van der Waals forces, and this kind of joining is known as a dispersive adhesion or adsorption. An adhesive joint is formed by using an adhesive between the adherends (Figure 1). [12]

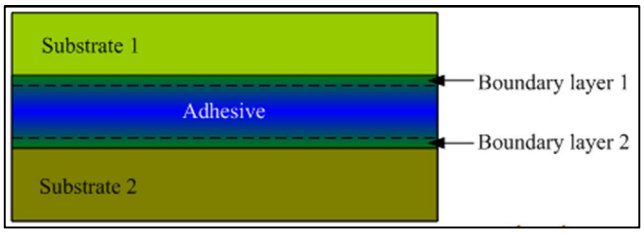

Figure 1 *Structure of the adhesive joint. Adopted from [13]*

There is an invariably increasing demand for the adhesives in the new kind of applications. The adhesive bonding may be used to join almost any types of materials together. The geometry or configuration of the materials to be joined is not so restrictive either. The adhesive joints are invisible, lightweight and spread the stresses over larger bond area. Also the fatigue properties of the adhesives are usually very good. For example with welding or soldering the surfaces are permanently changed by the thermal stresses whilst by using the adhesives the strains are dissipated over the whole surface without creation of the stresses. By adhesive bonding the pieces are not weakened as

happens with riveting, bolting or screwing methods in which the holes act as the stress concentrators. The adhesively bonded joints often weigh less than the mechanically bonded ones as only a small amount of the lightweight adhesive is usually needed to join the much larger adherends. [2, 11] If it is possible to design the adhesive joint so that the adhesive is stronger than the adherend then when a good joint is formed the adherend material fractures or ruptures before the adhesive. [2, 14]

2.3.1 Adhesion

One talks of adhesion when a measurable amount of the mechanical work is needed to separate the two surfaces of the different chemical composition or shape [2]. Adhesion may be defined as a molecular attraction between the surfaces of the components in contact; it is an attraction process between the dissimilar molecular species in a direct contact in such a way that the adhesive binds to the applied surface. Cohesion is a molecular attraction by which the particles of a component are united throughout the mass; it is an attraction occurring between the similar molecules. Thus adhesion is about the bonding of one material to another, due to a number of different possible interactions at the adhesive-adherend interface, whereas cohesion may be defined as the internal strength of the material due to the various interactions within that material. [15] A certain amount of energy is needed to separate the material's atoms or molecules to an infinite distance [11].

There are different theories of adhesion. A series of mechanisms have been recognised, each one having an appropriate part to play, either alone or in combination with the others. Such theories are for example mechanical interlocking, adsorption, chemical bonding, diffusion, electrostatic forces and weak boundary layers. [11, 16] An adhesive is a material that forms structural bond between two materials or components, adherends. Adhesion occurs when these two surfaces are held together. [17] In every situation involving an adhesive and adherend, the combination of the adhesion and cohesion determines the overall bonding effectiveness. [15]

With adhesion the surface has an important role. The first thing to consider is the surface roughness, more precisely the surface topography, which can be analysed for example with a probe or electron microscopy. When a good mechanical locking is chased a tortuous interface between the adhesive and surface is better than a smooth one. [11] Initial adhesion will be a function of the interaction of the surface forces and the mechanical properties of the contact. For the polymers the surface forces are

combination of the van der Waals-, coulombic- and hydrogen bonding forces. [18] Further, the material properties near the surface or interphase are not necessarily the same as inside the bulk material [17]. The ability of the polymer materials to conform to the minor surface imperfections coupled with a relatively low level of stored elastic strain will also facilitate a stronger adhesion. [18]

Material's surface attraction is referred to as surface energy, surface free energy or surface tension. A simple method for determining the surface energy of the material is through the use of the contact angle analysis, in which a drop of a liquid is placed on the surface of a solid and allowed to flow and equilibrate with the surface. [11, 17] Another method is the dynamic-contact analysis in which the wetting force on the solid is measured as the solid is immersed in or withdrawn from a liquid of known surface tension. The greater the attraction of the liquid to the solid surface the greater the measured force to pull out the solid material will be. [17] Also more modern methods for the surface chemistry, such as X-ray photo electron spectroscopy or static secondary ion mass spectrometry, may be utilised [11]. The measured energy of the adhesion is dependent on the ability of the interfacial bonds to sustain stress, as well as on the amount of the plastic deformation caused locally by this stress [2].

Wetting is an ability of a liquid to form an interface with a solid surface. The degree of wetting is evaluated as a contact angle (Figure 2). The contact angle is a function of the dispersive adhesion, which is an interaction between the molecules in the adhesive and those in the solid, and the cohesion within the adhesive. If there is a strong adhesion to the substrate surface and a weak cohesion within the liquid then there is a high degree of wetting. A smaller contact angle indicates more adhesion is present because there is a larger contact area between the adhesive and the substrate. It results in a greater overall substrate surface energy and a higher adhesion force (which is greater than the cohesive forces within the adhesive) between the adhesive and the substrate. [2, 15] A good surface wettability occurs with the contact angles less than 60° [19].

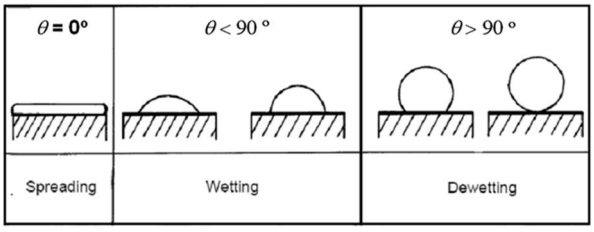

Figure 2 *Wetting of the surface [20]*

A clean surface allows good wetting, whereas the contaminants usually lower the surface energy. One talks about de-wetting (Figure 2) when the contact angle exceeds 90°. It may happen if the surface is contaminated or if the surface energy is low. Then the cohesion within the adhesive can exceed the adhesion between the liquid and substrate, and the liquid will form droplets on the substrate surface. Spreading enhances the macroscopic and microscopic contact between the adhesive and substrate. [15, 17]

As the bonding is dependent on the atomic arrangements and the chemical properties of the molecular conformation and the chemical constitution and diffusivity of the elements in each constituent, it follows that the interface between the different substrates has specific properties [2]. Often an adhesive bonded to an adherend has a modified molecular structure at the bonding interface. This interfacial region is known as the adhesion zone and it is characterized by the changes that arise from the bonding interactions. The transition zone, that is the region between the bonding interface and the bulk of the adhesive, is the area over which the chemical, mechanical and optical properties of the adhesive differ from those of the bulk adhesive (Figure 3). It varies in thickness, from few nanometres up to few millimetres, with the thickness depending on the nature of the substrate surface, the chemical composition and the physical characteristics of the adhesive and the curing conditions. [15] A strong joint occurs when this interfacial layer is strong enough to withstand the external stresses [19].

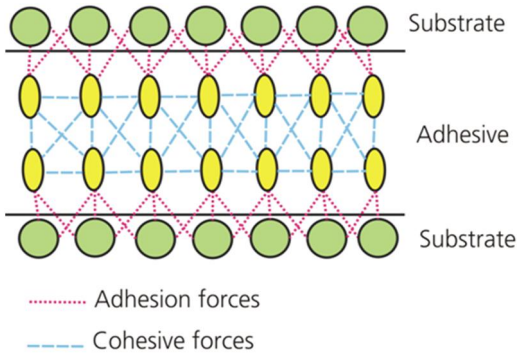

Figure 3 *Adhesion and cohesive forces [21]*

Adhesion is achieved through the molecular interactions between the adhesive and the adherend surface. The intermolecular forces produce a specific adhesion which can be divided into three types: dispersive adhesion, diffusive adhesion and chemical adhesion. With the dispersive adhesion bonding is partly based on the van der Waals forces whereas with the diffusive adhesion bonding based on the diffusion is involved too. Chemical bonding may be due to the formation of the stronger ionic or covalent bonds or the weaker hydrogen bonds and is known as the chemical adhesion. [12] A

further distinction is made between the weak intermolecular interactions and the strong chemical bonds. If there are chemical bonds within the adhesive joints, they can account for up to 50% of all interactions (although the long-term stability of these bonds is usually dependent on their resistance to moisture). In addition, the micro-mechanical adhesion can be involved in the overall adhesion phenomenon. In such case, the adhesive can effectively stick to a roughened substrate surface and thus increase the overall adhesion. It is not simply a matter of wetting and the rheological properties of the adhesive but there are other factors such as the electrostatic forces between the adhesive and the substrate or the adhesive's thixotropy. [15]

The cohesive strength is determined by the molecular forces: the chemical bonds within the adhesive material, the chemical bonds due to crosslinking of the polymer, the intermolecular interactions between the adhesive molecules, and the mechanical bonds and interactions between the molecules in the adhesive. These molecular interactions affect the properties such as consistency and viscosity of the uncured adhesive. When the adhesive cures, the solidification occurs through the bonds formed between the molecules in the adhesive, through formation of the new bonds and by the strengthening of the existing bonds. This overall process typically consists of crosslinking of the short chain molecules to form the longer chains and/or formation of three-dimensional networks of the molecular chains. [15]

With the chemical adhesion the adhesive and substrate can form a compound at their interface. The ionic or covalent bonds that are formed result in a strong bond between these two materials. A weaker bond is formed if there is hydrogen bonding between. [15] Usually the mechanical bonding and the attraction forces dominate between the adherend and adhesive. Although more rarely occurring covalent bonding is desired because it requires the greatest amount of energy to break when compared with the weaker interaction forces [17] such as van der Waals that affect in the dispersive adhesion. The van der Waals forces affect at short range and experienced by the couple of the molecule layers in the interface. About 99% of the work required to break the van der Waals bonds is performed once the joined surfaces are separated by more than a nanometre and, as a result, the effectiveness of adhesion due to the chemical or dispersive bonding is limited. [15]

Some materials may merge at the bonding interface by diffusion. Typically it happens when the molecules of both materials are mobile and/or soluble in each other. As a result the initial boundary disappears. However, the mobility of the polymers

strongly influences their ability to interact to achieve the diffusive bonding. The cross-linked polymers are less capable of diffusion because of their more restricted mobility. The diffusive bonding occurs when the atoms from one surface penetrate into an adjacent surface while still being bound to their surface of origin. Since the diffusive adhesion requires molecular interactions between the two surfaces, the greater the time that these two surfaces can interact, the more diffusion occurs and accordingly the stronger the adhesion is between the surfaces. [2, 11, 15]

2.3.2 Adhesives

An adhesive is a substance with viscoelastic behaviour and capable of holding the adherends together by the surface attachment. It produces a joint with high shear strength. [2] Every adhesive passes through a phase transition in the course of its use. This change from liquid to solid involves one of the general processes: loss of solvent, water or dispersant, cooling or chemical reaction. The adhesives may be classified to the solvent based adhesives, hot melt adhesives, reactive adhesives and pressure sensitive adhesives. The common adhesives used in the engineering applications are such as the anaerobics, epoxies, reactive acrylics, polyurethanes, reactive hot melt polyurethanes and special cyanoacrylates. All industrial adhesives contain a range of additives to modify the various properties. The additives are such as the promoters, inhibitors, modifiers and fillers and give the resin the properties and characteristics required in the particular application. [11, 16]

Some of the thermoplastic and thermosetting polymers are used as structural adhesives. They are tough, strong and reliable and can be applied to almost any combination of materials. The primary drawback of many polymers is their service temperature limitation. [2] The thermosetting polymers undergo an irreversible chemical cross-linking reaction and gain a three-dimensional structure in which the atoms are connected by the strong covalent bonds. [2, 6] Basically the curing reaction starts at the room temperature and may be accelerated with the heat and pressure. At first the viscosity and (elastic- and viscous) modulus of the liquid or paste form polymer are low. When curing starts the modulus increases sharply until the stabilisation is achieved and finally the polymer has solidified. Usually the curing of the thermosets is done for example by the heat, radiation, catalysts, activators or component reactions. Once these materials are set, the additional heating do not produce softening. A deformation would require breaking of the primary bonds. [2] The thermoplastic

polymers just melt on the application of the heat and pressure or dissolve in solvent, and harden by cooling or by evaporation of the solvent. This means these materials do not set permanently and the additional heating produces softening. [6, 17] The thermosetting polymers tend to be stronger than the thermoplastics and have usually lower ductility, higher modulus of elasticity, and poorer impact properties. As the thermoset molecules are densely cross-linked, their resistance to the heat and solvents is better than the thermoplastics have. [2]

The commercial adhesives are usually classified according to the polymer composition or the chemical type [19]. There are one- and two-component adhesive systems. The former systems are premixed, contain a specific condition activated hardener, such as the heat-, moisture- or oxygen activated curing agents, and do not need mixing before usage. While with the latter system the components, containing the curatives and cross-linkable resins, are supplied separately and must be mixed before use. [11, 22]

In the formation of the adhesive joint the adhesive must first be prepared and then spread over the pre-treated adherend surface. The adhesive system is in a paste or liquid state before and during application. Then it hardens and gains the full load-carrying abilities. The adhesives can be applied to the adherend by various methods manually or automatically. The manual methods are such as spatulas, rollers and glue guns whereas the automatic application is done for example by the roll coaters, flow coaters or extrusion installation. The other related process equipment are the drying and curing systems, ventilation systems, proper storage facilities and protective devices. [19, 22]

2.3.3 Surface pre-treatment

A vital consideration in any use of the adhesive bonding, before any bonding is attempted, is the state of the surfaces that are to be bonded [16]. A surface treatment increases the surface energy of the adherend. Without a proper surface preparation, even the best adhesive will not produce a durable and high strength joint. The pre-treatment cleans the adherend surface and may introduce the functional groups at the material surface yielding the potential bonding sites for the adhesive to promote wetting and chemical bonding. [17, 19] The used pre-treatment method depends on the adherend and the type of the surface contaminants. Generally the surface pre-treatment can be mechanical, chemical or electrical. The newer pre-treatment methods use for example flame, plasma, UV light or laser. [19] The physical methods include the removal of the

low cohesive strength material and the changing of the topography. The surface becomes also more effective for bonding. The pre-treatment is done for example by the solvent wipe and/or by the abrasion method such as sanding or blasting. The chemical methods are such as removal of the weak material, roughening and the introduction of the functional groups into the polymer. The chemical pre-treatment may be done for example by etching. Also electrochemical reactions, corona discharge- or plasma treatment may be used. [2]

Basically a surface treatment, which produces good bond durability, involves three steps: it thoroughly degreases the surface, it removes the existing surface layer to produce a chemically active surface, and it establishes a stable, active surface which will form the hydration resistant bond with the adhesive or primer. Each of the steps is essential and must be performed in the above mentioned sequence. The surface pre-treatment may be followed by the surface post-treatment such as application of conversion coating or inhibiting primer coating. [23]

2.4 Material failure

Material failure can be viewed as any change of the properties which makes the material functionally, structurally or aesthetically unacceptable. Such failure can be caused by the mechanical, thermal, chemical or other environmental influences such as oxygen, UV radiation or water. [6]

The linear elastic fracture mechanics can serve as the basis for the fracture analysis and testing. With the stress intensity factor approach the stresses and local strains are greatly increased at the tips of the defects in a material and serve as initiation sites for the structural failures. The main types of loading that give rise to the different fracture surfaces have been termed mode I, mode II and mode III and denote the crack opening, shearing and tearing (Figure 4). A mixed mode loading includes two or three of these modes simultaneously. [25]

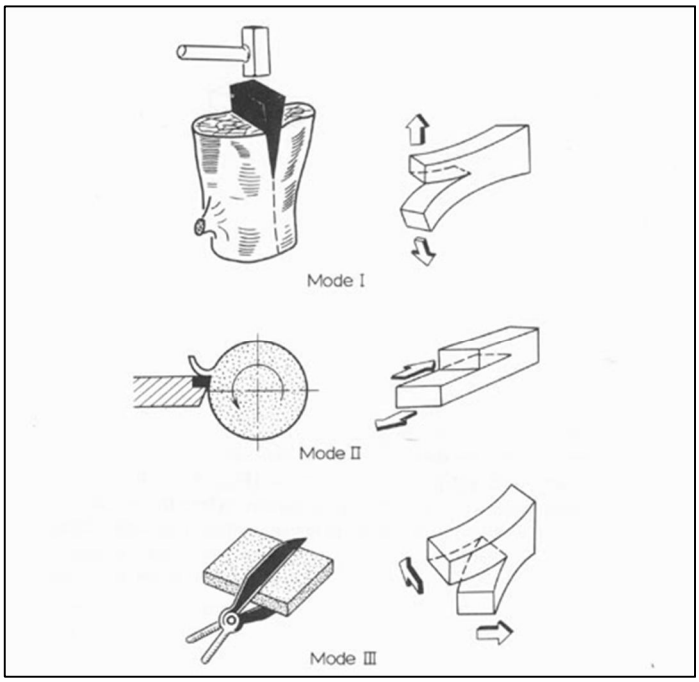

Figure 4 *Three modes of crack surface displacement. Adopted from [24]*

With the energy release rate approach it is stated that a crack propagates when the applied energy release rate reaches the critical value (known as the fracture energy) of the material. [25]

2.4.1 Failure of the polymer materials

In a linear elastic solid a fracture occurs as a combination of stress and crack. A fracture toughness is defined as a material property depending on the temperature, polymer grade, orientation and so on; the larger the value the tougher the material. Stress is material's internal resistance arising from the applied load. A deformation under stress is called a strain. From the failure point of view there are two general types of fracture: brittle and ductile [6].

A brittle failure usually occurs with the amorphous polymers below their glass transition temperature, T_g, and with the highly cross-linked polymers also in a creep rupture and fatigue above T_g. Typically it occurs at very small strains, 1% or below. With a brittle material the stress-strain curve has a constant slope until the point where the small microcracks form just before the failure. These small microcracks, crazes, are nucleated at the points of the high stresses such as the scratches, dust particles or other inhomogeneities. Crazing is directly related to the speed at which the component is deformed. At the high deformation speeds the crazes are small and form shortly before the failure. At the slow rates the crazes tend to be larger and occur early on during

loading. The high stress crazes form under the static load and do not pose an immediate danger to the polymer component. The crazes are irreversible and they imply a permanent damage within the material; once these have formed the material no longer obeys the law of linear viscoelasticity. When the modulus (stiffness) versus temperature curve and the crazing strain versus temperature curve are compared it can be seen that formation of the microcracks is inversely proportional to the stiffness of the material. [6] Crazing is a significant mechanism by which the polymer absorbs energy (which prevents the fracture). For the thermoplastics crazing may be considered a toughening mechanism, but for the thermosets crazing may be an undesirable phenomenon which by lowering the strength of the material can induce failure. [25]

A ductile failure takes place with the semi-crystalline thermoplastics at the temperatures between T_g and the melting temperature, T_m. At first the semi-crystalline polymer behaves like an elastic solid whose deformation is reversible. This takes place when the component's load is applied and released fairly quickly, without causing a permanent damage to the material and allowing the component to return to its original shape. If the load is increased or the process is slowed the stress-strain curve becomes non-linear and the microcracks form in the interface between the neighbouring spherulites. This is called stress whitening and is an irreversible process. By further deformation of the specimen the stress-strain curve reaches the yield strength beyond which the stress drops. Once the necking has occurred the specimen continues a long cold-drawing process where the spherulitic structure is deformed and broken up. Eventually the highly oriented regions have been formed within the polymer as the amorphous ties between the lamellae have been completely extended. [6]

A rather abrupt thermal softening of the glassy polymers leads to an uncontrolled thermally induced failure. This is a notable feature of the behaviour of the non-cross-linked systems where the molecular mobility and flow are not constrained by the crosslinking process or by the crystalline phases. When a polymeric contact reaches a temperature near to the glass transition or crystalline melting temperature there is a pronounced decrease in the Young's modulus and hardness. [26]

Due the viscoelastic nature of the polymers, they undergo a time- and temperature dependent response under the stress or strain conditions which may cause failures. Creep is a delayed strain response after a rapid application of stress. In a stress relaxation there is a subsequent decay of stress by the material after the rapid application of strain. [25]

A chemical attack to the polymers can occur for example via oxidation, solvation or molecular degradation. All adhesives absorb water more or less. [25] The ubiquitous nature of water combined with the ability to penetrate into the polymer structure poses the considerable problems [27]. Some polymers, especially the condensation polymers which evolve water during polymerisation (such as polyesters and polyamides), may be more sensitive to the humid or aqueous environments and therefore may more easily fail by the hydrolytic degradation if exposed to water. The effect of water depends on the relative humidity (RH). At lower humidities, for example less than 50% RH and 50°C, polymers may withstand for the longer periods without degradation, whereas at 100% RH and 50°C the joint strengths may fall 40-60% or more during the first 2-3 months (or less) and then level out. The water absorption begins by diffusion (or sometimes by capillary action), is followed by the water interactions with the polymer and finally the polymer degrades. Usually the moisture diffusion occurs in a Fickian manner, which means that after a certain exposure time an asymptotic value is reached as saturation is approached. [25] An elevated temperature usually makes the situation worse as diffusivity increases by elevating the temperature [27]. The water molecules may act as a plasticizer and plasticizing usually decreases the glass transition temperature as the modulus of the material reduces and the elastomeric range is shifted to the lower temperatures; for example the tear strength and the flexural strength decrease. The acidic and alkaline environments may cause degradation as well. With the polymer oxidation the major factor is the combination of oxygen as a reactant and heat as an energy source. The indicators of the chemical degradation are such as embrittlement, cracking, swelling, distortion and dissolution. Due to the chain scission and crosslinking reactions the strength decreases. [25]

2.4.2 Failure of the filled/reinforced polymers

The reinforced polymers have higher resistance to the crack initiated failures than the plain polymers as the reinforcement is able to arrest the crack propagation. The failure behaviour of the reinforced materials is more complex for example due to anisotropic nature in which case both the magnitude and orientation of the stresses are important. These materials can have a number of fibre orientations that is an important factor in the failure modes the material can undergo. The failure mode is a manner in which a system fails and is a result of a complex interaction of the factors which can give rise to material cracking, de-bonding or delamination, fracture, grazing and so on. The failure

modes can for example be filler/reinforcement, matrix or interface dominated. The degree of bonding between the reinforcement and the matrix has a substantial effect on the performance properties. The presence of the impurities or a non-uniform distribution of the fillers may cause an incomplete or uneven cure of the thermosetting resins that increases the failure probability. [25]

A polymer that usually fails in a brittle manner can be toughened by adding the filler particles. This increase in toughness is reflected in the stress-strain behaviour. The filler particles may lower the stiffness and ultimate strength of the material but increase its toughness. [6] The tougher polymer usually has also higher wear resistance than the brittle one. [7] The filler particles halt the propagation of the growing craze. The characteristic lengths of the crazes that form in such systems are only as large as a characteristic gap between the filler particles. This creates a system that has a large number of small crazes instead of a small number of large crazes. With the thermosetting polymers this effect is referred to the crack pinning. [6]

The failure of the filled material may begin at the interface between the filler and matrix and the breakage is generally referred to as de-bonding. The initial microcrack formation is reflected in a stress-strain curve by the deviation from the linear range of the elastic deformation and the failure is analogous to the microcracks that form between the spherulites. Also the thermal expansion mismatch between the materials can cause stresses that result in microcracking. The larger particles will act as the microscopic stress concentrators and lower the strength of the material. The reinforced polymers tend to be stiffer and less susceptible to the fatigue failure and also have the lower hysteretic heating effects that make them less likely to fail by the thermal fatigue. The fibre reinforced systems generally follow a sequence of events during the failure consisting of matrix cracking, debonding, fibre cracking and separation. The fracture by fatigue is generally preceded by the cracking of the matrix material which gives a visual warning of an imminent failure. [6, 25]

The presence of absorbed moisture and the tendency for the hygrothermal degradation is a limitation of many of the polymers as it causes the material failures and de-bonding in the polymer-reinforcement interface. The moisture uptake rate is temperature dependent and the higher temperature accelerates the degradation process. In addition the exposure of water has different effects depending on the specimen thickness, the type of the polymer or the reinforcement, the reinforcement orientation, the state of the interface and the manufacturing process. Also the defects in the material

usually increase the uptake rate. On the other hand the possible swelling may act as a crack closure. While the process of the moisture absorption from the surface occurs immediately on contact with the aqueous environment, the moisture flow into the interior of the material structure will usually be slow and may need weeks of exposure before a notable amount of water is absorbed. The diffusion of liquid into a material gives rise to the swelling and the formation of the (internal) stresses inducing the cracking of the polymer. The polymer-reinforcement interface may de-bond due to the chemical degradation of the interphase. For example the fibres may suffer cracking caused by the stress corrosion caused by the hydrolysis. [25]

2.4.3 Failure of the adhesive bond

The adhesive bond will fail if the adhesive separates from the substrate or there is an internal breakdown of the adhesive [15]. There are three basic ways how an adhesively bonded joint may fail. In one of them the failure is inside one of the adherends and means the structural failure is outside the adhesive joint. So it is a cohesion failure of the adherend. In another case the fracture is inside the adhesive layer, which is a cohesion failure of the adhesive. In the third case the interface between the adhesive and one of the adherends fails and that is an adhesion failure (Figure 5). Of course the failure may be a combination of the foregoing. [23]

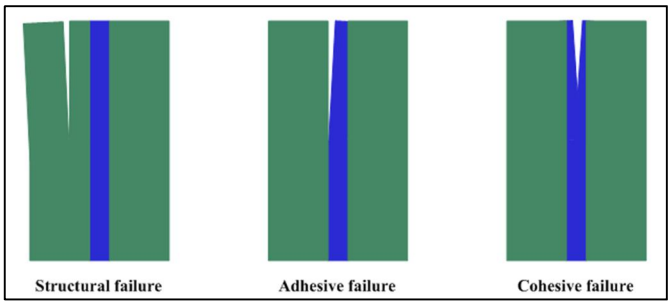

Figure 5 *Failure mechanisms of adhesive bonding. Adopted from [13]*

If the adhesive is weaker than the substrate the failure is cohesive and the properties of the adhesive determine the properties of the joint. [2] If the failure is within either of the adherends, the joint is more than sufficiently strong. In a case the failure is within the adhesive then a consideration must be given to whether an alternative adhesive or maybe different bonding geometry would be a better choice. A very considerable proportion of the failures, however, appear to be at one of the interfaces. [16]

The cohesive bond failures result in a fracture of the adhesive and are characterised by the presence of the adhesive material on the matching faces of both adherends. The

failure is usually by shear, but the peel stresses or a combination of shear and peel may also cause the cohesion failure. The shear stresses in an adhesive bond are not uniform. The higher shear stresses arise at the ends of the joint and are lower in the centre. The cohesion failures found in service are typically caused by the poor joint design although the excessive porosity, poor curing, cracks or voids may also result in the cohesion failure (Figure 6). [23, 14]

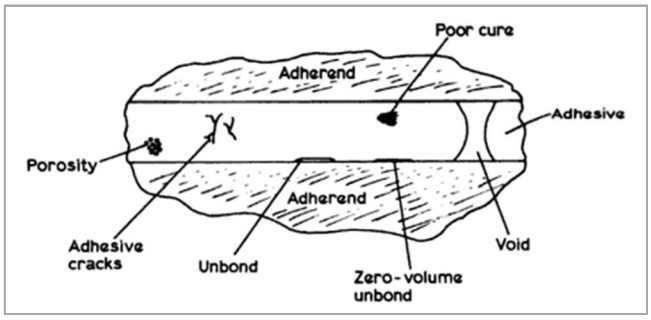

Figure 6 *Typical defects in an adhesive joint. Adopted from [28]*

Assuming that the adhesive was correctly formulated and cured only the true cohesion failure indicates that the full strength of the adhesive bond was achieved [29]. The adhesive bonds are very fatigue resistant and only under certain circumstances will a cohesion failure be caused by the fatigue. [23]

The basic theories of the adhesive bonding that attribute the adhesive bond strength are the surface roughness, diffusion of the adhesive into the bonding surface, weak molecular attraction and the adsorption theory, that is a combination of the weak molecular attraction and the chemical bonds between the adhesive and the adherend. The strength and fatigue tests may show that the bond strength is adequate and that the structure has a sufficient fatigue resistance at the time of testing. Still they do not verify that the component will be durable throughout its service life. [23] The high static shear strength in a bonded joint may not translate to the good performance under the load and/or aggressive environment. [27].

Water is one of the aggressive environments into which the adhesives may be exposed. The critical water concentration is reached when the significant losses of the strength occur. It depends on the used material, temperature and stress. Moisture may diffuse through the permeable adhesive or adherent or it may travel along the interface and migrate by the capillary action through the cracks and crazes. Water causes weakening once entered a joint, though the amount of water in the adhesive layer does not have a direct relation to the joint strength. Water may work as a plasticizer which may lead to swelling or material softening and then the strength and stiffness are lost.

Also the secondary bond disrupting, cracking, crazing or hydrolysing may happen. An inadequately prepared surface may be chemically active and form a high number of chemical bonds to provide the adequate short term strength. However, if the surface is not resistant to hydration, the bond strength will gradually deteriorate. For example the combination of the raised temperature, water and fatigue loading is a very demanding environment for the adhesive joint. [2, 23, 27] The causes of the adhesion failure may be various; for example usage of an inappropriate surface preparation technique that is unable to produce a chemically active surface (resistant to hydration), contamination of the surface during the production process, or the adhesive may cure before the bond is formed. [23]

Care is required to correctly assess the surfaces which show a mixed adhesion and cohesion failure. For example a bond which is susceptible to hydration or to other chemical attack at the interface, the interfacial degradation occurs over a period of time and the bond strength degrades. If this partially degraded bond is subjected to a high load then the weakened interface may fail and overload the adhesive in the regions which have not fully degraded. This then gives the appearance of a mixed mode failure. [23, 29]

3 THEORY OF WEAR

The process of wear may be variously defined but most generally it is quantitatively measured in terms of the mass or volume loss from a sliding or eroding contact [26]. Wear is defined as damage to a solid surface or a removal of material from one or both surfaces due to the relative motion between this surface and the contacting substance or substances. This removal may or may not result in a net system weight loss. The latter means the material may have been transferred from the one counterface to the other, or may have been ploughed out. [10, 17] The changes in the surface layer arise from the mechanical stresses, temperature and/or chemical reactions. The polymers due to their specific structure and mechanical behaviour are more sensitive to these factors. [30]

An element of the chemical degradation is present in all wear processes. It ranges from a mild chain scission, for example a gentle fatigue abrasion, to a gross decomposition under intense loading. Even in the most favourable circumstances there is doubt as to the precise role played by the chemical reactions in the overall wear process. [18]

Wear is not a material property but a systems response. Wear is supposed to occur when a strain has accumulated to a critical value causing a fracture. In the early stage wear is caused by the brittle fractures in the surface grains and in the later stage by the tribochemical reactions. Mechanical wear describes wear mainly governed by the processes of deformation and fracturing. The deformation process has a substantial role in the overall wear process of the ductile materials whereas the fracturing process has a major role with the brittle materials. [31]

The local temperature at the interface may be substantially higher than that of the environment and may be enhanced at the asperity contacts by the transient hot-spots. The temperature exerts an influence on wear of the polymers. These mechanisms are the basis for the wear process, yet the great diversity of the mechanisms and their interrelation makes it impossible to rigorously classify these processes. [30]

3.1 Materials mechanical properties and wear

The mechanical properties of the contacting materials should be taken into account at any scale level but depending on this level such parameters as Young's modulus and hardness can differ not only in magnitude but also in their physical interpretation. This deformation is accompanied by the dissipation of the mechanical energy depending on the deformation mode, sliding conditions, rubbing materials, scale level of the mechanical properties, environment, and the other factors. [30] The microstructures and properties of the polymers are manipulated by cross-linking and by adjusting the molecular weight and the degree of crystallinity. More dramatic changes are possible by blending or adding the fillers or reinforcements. [3]

The basic material properties such as ultimate strength, yield strength, endurance limit in fatigue, creep strength, ultimate strain, creep strain limit, elastic modulus, creep compliance, dynamic modulus and glass-transition temperature affect the wear process. Also the operating temperature and -environment should be taken into account. [17]

Strength is the material's resistance to the external load; the stronger the material the greater load it withstands. Stiffness or rigidity is the capacity of a system to sustain load without an excessive deformation and is measured by the Young's modulus. Toughness refers to the energy amount required to fracture a specimen thus it is the material's ability to withstand the plastic and elastic deformations without a catastrophic failure and it can be increased through toughening, which enhances resistance to fracture, impact, and thermal stresses. The higher toughness means the material absorbs more energy and has therefore a better resistance to the propagation of a crack. Hardness is the ability of a surface to resist a static contact pressure. [3, 11] Impact strength is the material's ability to absorb energy under the impact conditions or the energy absorbed into the material before a failure. One measure of the impact strength is the modulus of toughness (that is the area under the stress-strain curve of tensile test conducted at high strain rate, Figure 7). The thermoplastic polymers tend to have a higher modulus of toughness than thermosets due their relatively high elongation. [17]

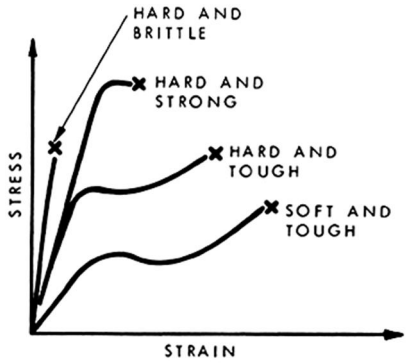

Figure 7 *Tensile stress-strain curves for the different types of materials [32]*

Ductility refers to the maximum strain in the stress-strain curve. A brittle material undergoes little or no plastic deformation before a failure and breaks more easily under tension than under compression. [12] Under specific conditions such as at low temperatures and at very high deformation rates even the most ductile materials can fail in a brittle manner at very low strains. A high rate of deformation leads to a complete embrittlement of the polymer which results in a lower threshold of elongation at break. [6]

The modulus versus temperature diagram is a useful description of the mechanical behaviour of the polymers. The behaviour is different for the amorphous, semi-crystalline and cross-linked polymers (Figure 8). [6]

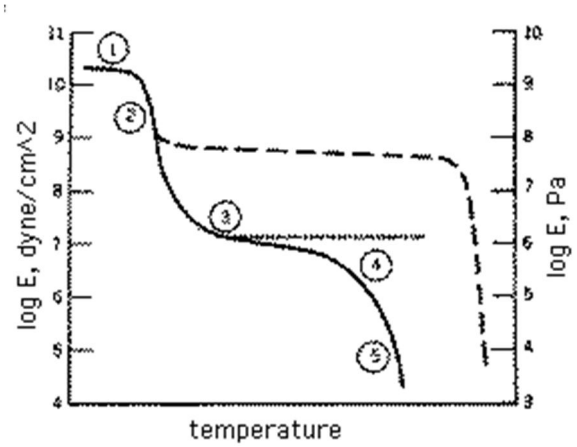

Figure 8 *Modulus versus temperature graph for amorphous, cross-linked (dotted line) and semi-crystalline polymer (dashed line), 1.Glassy region, 2.T_g-region, 3.Rubbery plateau, 4.Rubbery flow region and 5.Liquid flow region [33]*

Under static fatigue or during creep a loaded polymer component will gradually increase in length until a failure occurs. The component is loaded under the constant

stress, constantly straining until the material cannot withstand further deformation causing it to rupture. At high stresses the rupture occurs sooner than at the lower stresses, or may not happen at all if the stress is low enough. Time to fail depends inter alia on the temperature, load, manufacturing process and environment. [6]

Dynamic loading of any material that leads to a failure after a certain number of cycles is called fatigue or dynamic fatigue. A cyclic or fluctuating load will cause a component to fail at much lower stresses than it does under the monotonic load. Fatigue with the polymers is strongly dependent on the environment, temperature, frequency of loading and the surface. Under fatigue circumstance the material performance is characterised by the cyclic stress versus cycles to failures curve (S-N-curve). [6] A failure under repetitive loading usually may happen suddenly after a long service. [25]

3.2 Friction and wear

Friction is a tangential resistance to sliding of the relative surfaces. The coefficient of friction is obtained when the tangential resistive force is divided by the normal load. The frictional force arises from the combination of the adhesion force between the real area of contact and the deformation force needed to plough the asperities of the harder surface through the softer one. The static friction force is the tangential force required to initiate the bulk sliding. The dynamic friction force is the tangential force required to maintain sliding at non-zero velocity. The static friction force can possess a time dependence caused by the viscoelastic effects experienced during the contact. As the dwell time between the two surfaces in contact increases, the area of contact can increase because of creep, and the strength of this contact from the attractive forces can increase. [17, 34]

The laws of friction state that the friction force is proportional to the normal load, the friction force is independent of the apparent area of contact and the friction force is independent of the sliding velocity. Although many materials obey these laws the reliability of them varies much. For example the polymers do not follow these laws well. [34]

The contact area between the sliding surfaces is said to be independent of the applied force. Yet the real contact area is dependent on the surface asperities and their shape. On the contact surface an elastic, plastic or viscoelastic deformation of the asperities may happen. In consequence the load and sliding speed influence on the friction

coefficient and the wear rate. So, increasing of the normal load influences both the deformation and the adhesion components of friction. When the asperities deform, the true contact area becomes larger with an increase of the friction forces. Also the strength of the adhesion can change. For the most polymers the overall effect consists in a decrease of friction with increasing of the normal load. However in some cases the balance of adhesion and deformation contributions can produce an increase of friction (depending on for example the surface energy of the polymer). The sliding speed affects the coefficient of friction due to viscoelasticity of the polymers and through its effect on the frictional heating. When a polymer melts its friction usually decreases. The sliding speed and temperature of the contact have significant effects on this relation. [30, 35, 36]

The friction coefficient and wear resistance are not real material properties but depend on the system in which these materials function [5]. A single material does not possess a coefficient of friction, which can only exist between two materials. The coefficient of friction depends on many parameters of the mating surfaces, such as geometry, surface finish and material properties. The friction force and thus the coefficient of friction have many functional dependencies, such as temperature, velocity, relative humidity, surface roughness and presence of lubricants. The surface roughness has a complex effect on both friction and wear. [17]

In the sliding systems the heat generation results in increased temperatures of the mating materials which affect the material properties and thus friction and wear. The temperature's types of concern are bulk and flash temperatures. Both types can result in a melting of the counterface materials, though the bulk melting is more obvious and results in a catastrophic failure of one or both counterfaces. In general, the mating condition is not perfect and the load is carried by an area less than the real area of contact. This area can approach the dimension scale of the asperities. When this occurs, all frictional energy is dissipated in a very small volume of material and the instantaneous temperature can flash up from 50°C to 100°C above the bulk interfacial temperature. [17]

3.3 Interfacial and cohesive wear

Friction and wear of the polymers differ from that of the metals or ceramics mainly because of the chemical and physical structures and the surface and bulk properties. The frictional work causes damages and subsequent wear, which involves the surface and subsurface deformation. These mechanisms have been classified as the interfacial and cohesive wear processes. This makes a distinction between the mild deformations of the cohesive wear and the more energy intense interfacial wear. With interfacial wear the frictional energy is dissipated mainly by the adhesion between the surfaces while the cohesive wear results either from the abrasion associated with an elastic or plastic deformation or from the fatigue crack growth in the deformed region. Thus the cohesive wear is subsurface or bulk wear and the damage is produced deeper into the material than only at the interface. Figure 9 describes this difference more in detail. [26, 34]

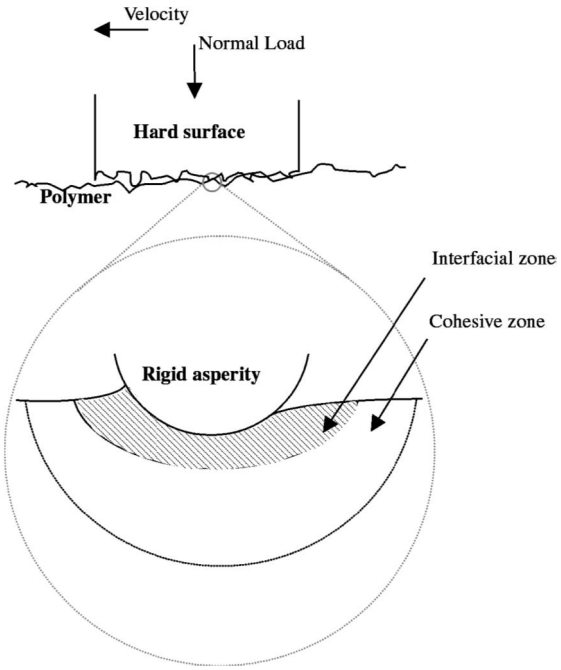

Figure 9 *Two-term model of the wear processes [26]*

With interfacial wear the material removal results from the processes occurring within a narrow region adjacent to the interface and includes the mechanisms of adhesive or transfer wear and chemical erosive wear. Adhesive wear involves the transfer of the polymer to the harder counterface and its subsequent removal as a wear debris. Yet not all polymers show this type of adhesive wear; for example in case no transfer film is formed this wear occurs by the fatigue or abrasion. The frictional work is dissipated in a smaller region and at higher energy density and the rates and extent of

the surface deformations are greater than those which exist in the cohesive wear. This often creates a significant increase in the local temperature. The frictional work originates from the adhesive forces which result from the contacting surfaces. These adhesive forces may generate a localised plastic surface deformation and a transfer of relatively non-degraded material to the counterface. Sometimes the localised deformations with the associated temperature rises produce chemical degradation and the transfer of degraded material. [18, 35]

With cohesive wear the frictional forces produce the tractive stresses which induce abrasion and fatigue wear and are manifested in the formation of the cracks at the surface or the subsurface faults within the relative thick zone. The wear mechanisms are controlled by the cohesive strength, toughness or fatigue properties of the polymer. [18, 34]

3.4 Wear modes

The various modes of wear form a source of heavy economic loss in the industrialized countries. The most general modes of wear are adhesive, abrasive, fatigue and erosion mode. [10,17] Wear can be also defined according to the motion, for example rolling-, sliding-, impact-, fretting- and cavitation wear, though these are based on the same mechanisms as the wear modes mentioned formerly [31].

The mechanism of wear is very complex. The real area of contact between the two solid surfaces compared with the apparent area of contact is invariably very small, being limited to the points of contact between the surface asperities. The load applied to the surfaces will be transferred through these points of contact and the localised forces can be very large. The material intrinsic surface properties such as hardness, strength, ductility and work hardening are very important factors for the wear resistance, yet other factors like surface finish, lubrication, load, speed, corrosion, temperature and properties of the opposing surface are equally important. [37]

The microstructure of the contact surfaces changes as a result of wear. The wear particles agglomerate with time and cover the wear surfaces. Any initial wear mode may change to another wear mode in the process of the repeated contacts. It is important in a wear rate prediction to consider the critical condition for the transition of the wear mode from one to another. It is also important to remember that this transition differs substantially depending on the materials used. [31]

3.4.1 Abrasive wear

Abrasive wear is the most common cause of failure in the industrial applications. It plays a major role in 50% of all wear failures [38] and has a contribution of at least 60% of the total cost due to wear [10]. Abrasive wear starts immediately at the beginning of the sliding motion. [17] The wear mechanism is basically the same as in machining, grinding or polishing that are used for shaping materials [37]. Abrasion displays the scratches, gouges, and scoring marks on the worn surface, and the debris produced by the abrasion frequently take on the appearance of the fine cutting chips. [30]

There are two distinct modes of deformation when an abrasive particle acts on the plastic material. The first mode is grooving/ploughing, in which a prow is pushed ahead of the particle, and the material is continually displaced sideways to form the ridges adjacent to the developing groove and no material is removed from the surface. The second mode is named as cutting and all the material displaced by the particle is removed as a chip. [30]

Two-body abrasive wear occurs when one surface, which is usually harder than the second, ploughs or cuts the material away from the second and the cutting points are embedded in the counterface. Some asperities produce ploughing while the rest shows cutting depending on the two controlling factors: the attack angle of the particle and the interfacial shear strength expressed as the ratio between the shear stress at the interface and the shear yield stress of the plastically deformed material. The two-body abrasion often changes to a three-body abrasion as the wear debris with the loose hard particles starts to act as an abrasive between the two surfaces and grooves both of the surfaces. The three-body abrasive wear has been found to be about ten times slower than the two-body wear since it has to compete with the other mechanisms such as the adhesive wear and the slower mechanisms of material removal are involved. [30, 37, 39]

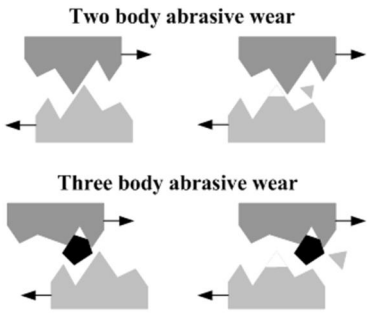

Figure 10 *Abrasive wear [40]*

As the abrasion involves tearing away of the small pieces of materials, therefore for example tensile strength, fatigue life, brittleness, toughness and hardness are important factors in determining the wear characteristics [10].

Moisture has a strong influence on the abrasive wear rates. Usually the rates increase with the moisture content, but there are occasions when a contrary effect occurs**.** The grit may either be just sufficiently weakened by the moisture to produce a larger number of new cutting edges, or severe grit weakening may occur, causing the disintegration of the grits into the non-abrasive fine particles. For the same abrasive and worn material, the two-body abrasive wear rate may increase with humidity while the three-body abrasive wear rate may either increase or decrease. [39]

3.4.2 Adhesive wear

For adhesive wear to occur it is necessary for the surfaces to be in an intimate contact with each other. Adhesive wear is produced by the formation and subsequent shearing of the welded junctions between the two sliding surfaces. [37] An adhesive wear process evolves in formation of the adhesion junction. A transfer of material from one surface to another occurs due to the localized bonding between the contacting solid surfaces. The processes associated with the other wear types, such as fatigue and abrasion, accompany the adhesive wear. [30]

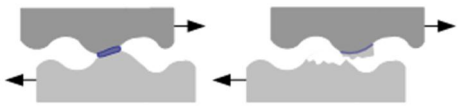

Figure 11 *Adhesive wear [40]*

Adhesive wear starts immediately at the beginning of the sliding motion [17]. When the two surfaces are brought into a contact, the surface forces of attraction and repulsion act between the atoms and molecules of the two approaching surfaces. Due to these forces the bonds formed between the contacting surfaces are followed by the junctions developed on the real contact spots. The formation and rupture of the junctions control the adhesion. For the majority of the polymers the van der Waals and hydrogen bonds are typical. Under the favourable conditions the two approaching atoms are linked together by a common proton providing a strong and stable compound. [30]

In general, the interfacial junctions, their formation, growth and fracture are influenced by the nature of the surfaces, the surface chemistry and the stresses in the surface layers. The interfacial junctions together with the products of their fracture and the highly deformed layers where shear deformation is localized are named as a third body. This term implies that the polymer involved in the friction process may possess the properties, which differ drastically from its bulk properties. [30]

3.4.3 Fatigue wear

Fatigue wear occurs as a change in the material state due to combination of the repeated stress and the initial crack. Its characteristic feature is an accumulation of the irreversible changes, which give rise to the generation and development of the cracks. The initiation of the fatigue cracks is assisted by the defects, such as scratches, marks or pits on the surface, or impurities, voids or cavities in the sub-surface region, which all are responsible for the stress concentrations. Both the surface and sub-surface cracks which open due to the repeated stressing will gradually grow, join, cross each other and meet the surface until the wear debris is detached after a certain number of stressing. [30]

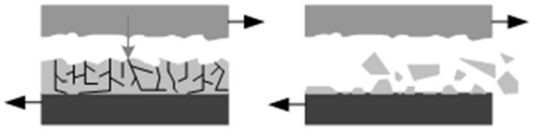

Figure 12 *Fatigue wear [40]*

A similar process takes place at friction accompanying nearly all wear modes. A contact undergoes cyclic stressing at rolling and reciprocal sliding. In addition, each asperity of the friction surface experiences sequential loading from the asperities of the counter surface. As a consequence, two varying stress fields are brought about in the surface and sub-surface regions. These fields are responsible for the material fatigue in these regions. It leads to the generation and propagation of the cracks and the formation of the wear particles. This process is named as the friction fatigue. Unlike the bulk fatigue, it spans only the surface and sub-surface regions. The loss of material from the solid surfaces owing to friction fatigue is referred to as fatigue wear. [30]

A subset of fatigue wear is delamination wear in which a crack propagates parallel to the surface until it reaches the critical length. At that point a flock of material is separated from the surface. [17]

3.4.4 Erosive wear

Erosive wear is caused by the impact of the particles of solid or liquid against the surface of an object. In common with the other forms of wear, the mechanical strength does not guarantee the wear resistance. Thus a detailed study of the material characteristics is required for wear minimization. The term erosive wear refers to an unspecified number of wear mechanisms which occur when the relatively small particles impact against the components. Most erosive agents are conveyed by a medium such as water or air. A mixture of the erosive particles and liquid medium is known as a slurry. The characteristics of the medium have a strong effect on the final wear rate. The factors related to the bulk properties of the medium are viscosity, density, turbulence and the microscopic properties such as corrosivity and lubrication capacity. [39]

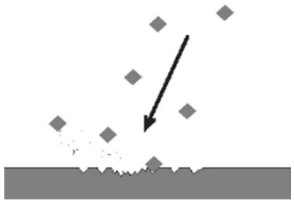

Figure 13 *Erosive wear [37]*

The properties of the eroding particle are significant and are relevant parameters in the control of this type of wear. The speed of the erosive particle has a very strong effect on the wear process. At very low speed the stress at impact is insufficient for the plastic deformation to occur and wear proceeds by the surface fatigue. When the speed increases it is possible for the eroded material to deform plastically on the particle impact. The size of the particle is also of considerable relevance and most of the erosive wear problems involve particles between 5 - 500 µm in size, although there is no fundamental reason why the particles should be limited to this size range. The angle of impingement effects on the wear rate as well. For the ductile materials the wear rate is usually highest around 30° whereas for the brittle materials the highest wear rate arise around 80°-90°. The hard particles cause higher wear rates than the soft particles and the sharpness of the particle also accelerates erosive wear. [39]

3.4.5 Other wear modes

When the operating environment becomes very severe and violent, the wear mode changes from abrasive to impact wear. Yet the process may also include the other wear mechanisms. Impact wear can be defined as wear of a solid surface due to percussion, which is a repetitive exposure to a dynamic contact with another solid body. Impact wear is wear of the surfaces under impacting conditions, when the two surfaces contact with the high relative velocities normal to their interface. The impact energies are typically several orders of magnitude higher than the corresponding energies for example in erosion wear. Impact wear can be further divided into two different modes. With one-body impact wear one of the mating surfaces is prone to greater wear than the other and the faster wearing surface is the component of the primary concern. With two-body impact wear, wear of both surfaces needs to be monitored. [38]

Fretting is a small amplitude oscillatory motion, usually tangential, between the two solid surfaces in contact. Fretting wear occurs when the repeated loading and unloading cause the cyclic stresses which induce a surface or subsurface break-up and loss of material. Vibration is a common cause of fretting wear [37]. The process of fretting is a good example of the importance of the debris accumulation and the debris expulsion from a contact zone. Again, the problem revolves around the imposed complexity of the sliding motions and the details of the specific actions of the interface shear fields [26]. Fretting wear differs from the other forms of wear in two aspects: the very low relative velocity of the contacting surfaces and the fact that the most parts of the contacting surfaces are never brought out of contact. Fretting produces a considerable amount of debris, known as third body, which does not easily escape from the contact and plays an important role in the wear of materials. [41]

The characteristic feature of cavitation wear is the cyclic formation and collapse of the bubbles on a solid surface in contact with a fluid. Wear progresses by the formation of a series of holes or pits in the surface exposed to cavitation. [39] Chemical wear describes wear governed mainly by the growth rate of a chemical reaction film, which is accelerated mechanically by friction. Therefore, chemical wear is called tribochemical wear. Thermal wear describes wear governed mainly by the local surface melting due to the frictional heating [31].

3.5 Wear of polymeric components

The processes of wear are not so well understood and the subdivision of polymer wear is no exception. A broad knowledge of the mechanical and chemical properties of the polymers, coupled with the probable conditions existing in the contact region, provides a predictive framework. [18] The major problems in the wear prediction are the undefined roles and the mechanical properties of the third body and the fact that polymers show a variety of mechanical responses under even a slight variation in the thermal or mechanical stress conditions. Besides, there is always an overlap of different wear mechanisms in any particular wear process. [26] In general, the factors influencing the polymeric tribochemical reactions are the chemical composition and the molecular structure of the polymer, the friction condition, such as speed, load and contact form, and the environmental substances [42]. Polymers show very low surface free energies and show viscoelastic behaviour. This effects in substantial tribological differences when the adhesive and mechanical components of the friction force are considered as the polymers can be easily modified both on surface and in bulk. [35]

The laws of friction are valid for some polymers tested under certain conditions. Thus the friction coefficient remains practically constant at load in the certain load range. But then outside this range the proportionality between the friction force and the applied load breaks down. In the range of moderate loads the friction coefficient may decrease with increasing the load and such behaviour may be explained by the elastic deformation of the surface asperities. On the other side of the range, the friction coefficient may increase with increasing load which is often explained by the plastic deformation of the asperities in contact. The load can change the temperature of the viscoelastic transitions in polymers and thereby vary the mechanism of friction. Though it is agreed that the friction force is independent of the sliding velocity still the complex relationships between friction and sliding velocity are observed. Such relationships can be connected with the viscoelastic behaviour of the polymers. In the range of the low velocities, the viscous resistance in the contact zone increases with increasing velocity. When the contact pressure is high, the abnormal viscous flow is observed. The flow leads to a sharp rise of viscosity due to the velocity increase. In the range of the high velocities, the elastic behaviour is prevalent in the contact zone and the friction force depends only slightly on the velocity or it decreases with the velocity. In addition, the duration of a contact is short at the high velocity leading to a further decrease in the

friction force. The friction force and sliding velocity relationship depends essentially on the temperature. When the tests are conducted near T_g, which allows a high mobility of the polymer segments, the sliding velocity has a pronounced effect on friction. At the lower temperature when the segments of the main chain are frozen friction is almost independent on the sliding velocity. [30]

Polymers can fail in fatigue under repeated loading. The stress amplitude of the fatigue fracture is significantly lower than that required for the tensile fracture. The causes of the fatigue failures are the mechanical crack initiation and propagation, and heating resulting from the internal energy dissipation and consequent softening. Because of the heating the stiffness decreases and the strain under constant stress cycling increases with time. [17, 25] The thermoset polymers show higher fatigue strength than the thermoplastics and the obvious cause is their greater rigidity. Even more important is the lower internal damping or friction which reduces the temperature rise during testing. The heat generation is caused by the combination of the internal frictional or hysteretic heating and the low thermal conductivity. If the frequency or the stress level is increased enough the temperature will rise to the point at which the specimen softens and ruptures before reaching the thermal equilibrium. This is termed as thermal fatigue. [6]

The abrasive wear behaviour of the polymeric material is complex. There is a need to understand the basic phenomenon of the two- and three-body abrasion and the movement pattern of the dry and loose abrasive particles. [10] A wear process is controlled by the material transfer which is a very characteristic phenomenon in the polymeric contacts. The transfer of the polymer material onto a counterface is initiated by the local strong adhesive bonds of the rubbing surfaces. The cohesive strength of the material is an important parameter. [35] If the interfacial bonding is stronger than the cohesive bonding of the weaker material, then this material is fractured and the polymer transfer takes place. Otherwise the fracture occurs at the interface. Usually with the polymers the surface forces and the forces acting between the polymer chains are nearly equal and a fracture often occurs in the bulk of polymers. [30]

When certain polymers are slid over the clean and smooth counterface the adhesion between the polymer and the counterface is of sufficient magnitude to inhibit sliding at the original interface. Instead the junctions rupture within the polymer itself and a layer of polymer is deposited upon the counterface in the form of a more or less coherent transferred layer. The subsequent traversals of the polymer over this film remove the

transferred layer which is in the end displaced from the contact. A further layer is deposited, the process repeats and the polymer surface is gradually worn away. [18]

The transfer layers, if they occur, are not immediately related to the chemical or physical composition of the host polymer. The transfer material does not correspond to what may be described as an original polymer but to a degraded form. In the interfacial wear process (Figure 14) first an initial contact of the two surfaces happens. Secondly a running-in process happens, during which the deformable polymer molecules are gradually transferred to the harder counterface as a third body. Thirdly a steady state wear process is achieved, in which the wear and friction phenomena are influenced mainly by the shear and adhesive properties of the transferred film. [26]

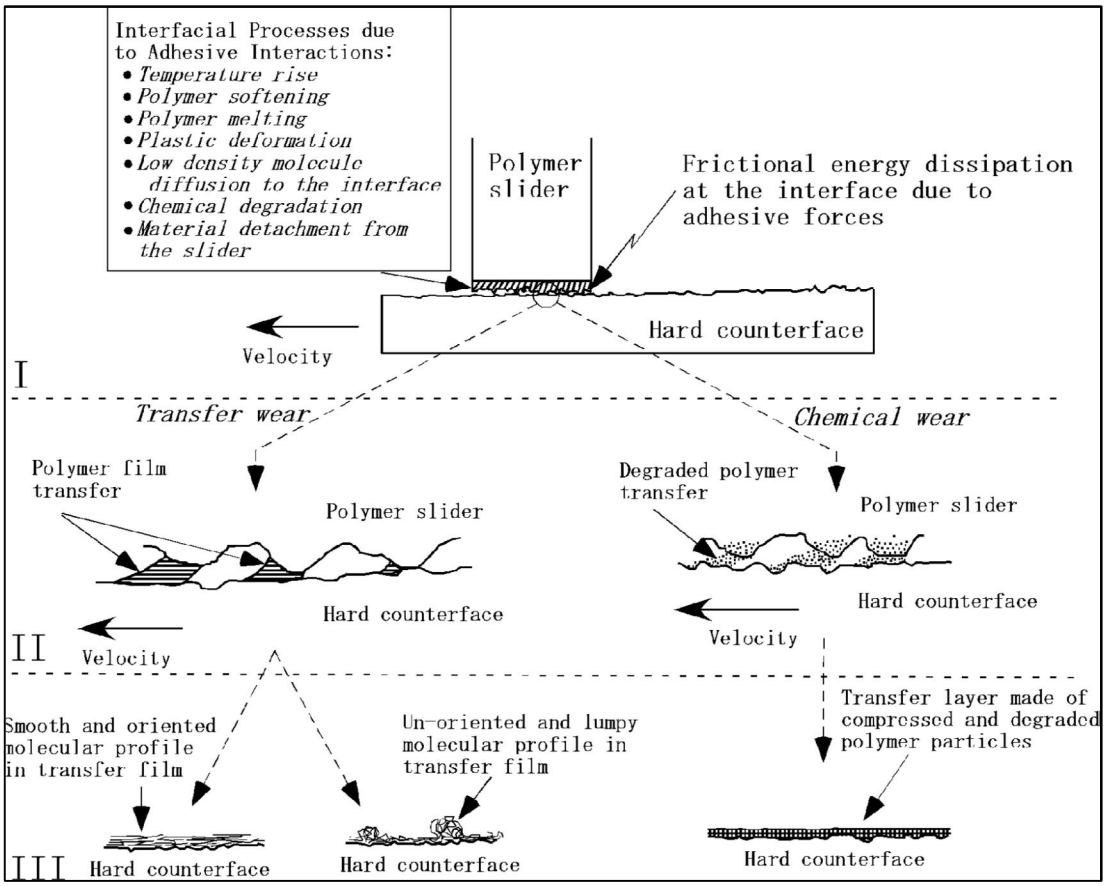

Figure 14 *Description of the interfacial wear process [26]*

If the polymer molecule chains can slide over each other easily and the transfer film is chemically bonded to the counterface forming strong adherence, then the transfer film is difficult to destroy. The chemically bonded points between the transfer film and counterface increase gradually as the rubbing goes on. Then the adhesive strength of the transfer film to the counterface and the transfer film area both increase. [42]. A transfer

film formed during the friction process can effectively improve the tribological condition of the polymer and reduce wear. [35]

Polymers as viscoelastic materials are very sensitive to the frictional heating. Some processes with their molecular mechanism relating to the transformation of the mechanical energy into heat can proceed via plastic deformation, hysteresis, dispersion, and viscous flow. Another source of heat can be attributed to the origination and breakdown of the adhesion bonds. [30] The frictional heat raises the temperature of the friction surfaces, which leads to relaxation of the polymer molecule chains. The molecules at the polymer surfaces are subjected to the mechanical compression, tension and shear and are deformed (or even broken) at different positions in the molecule chains, producing the different molecule radicals. The highly active radicals are able to react with the chains, giving rise to a series of new chain breakage events, or can polymerize with the other radicals to produce the new polymer molecules. [42]

Fretting wear of the polymers is essentially a process of adhesive transfer, plastic deformation, plastic flow and abrasion that are determined by the structure and the related properties of the polymeric materials such as chain flexibility, chain interactive ability, aggregate state structure and surface stiffness. The thermal effect is quite important factor as the production of the frictional heat at the interface and the thermal resistance of the polymeric material strongly affect the fretting wear process. [41]

A feature of the glassy polymers is that they do not transfer the coherent films of relatively degraded material to the counterface during sliding. If the frictional heating is substantial T_g of the polymer is exceeded and a gross surface melting occurs with an accompanying gross transfer of the material to the counterface. The rate of wear then shows a substantial increase in magnitude. [18]

3.6 Wear of composite/hybrid materials

The theoretical prediction of polymer wear is not completely resolved. For the polymer composites, the problem is further complicated by the factors such as the filler/reinforcement and matrix bonding properties and the role of the fillers in the third body. [26]

One of the traditional concepts for the improvement in the friction and wear behaviour of the polymeric materials is to reduce their adhesion to the counterpart material and to enhance their hardness, stiffness and compressive strength. This can be

achieved quite successfully by using the fibres or fillers. The behaviour is affected by the factors such as the type, amount, size, shape, and orientation of the filler, the matrix composition and the conditions such as load, speed and temperature. The size of the particles plays an important role in improving the wear resistance and the other mechanical properties. Reducing the particle size to a nanoscale level is assumed to reach a significant efficiency. It is of great importance that the fine particles are uniformly dispersed rather than being agglomerated in order to yield a good property profile. [5, 42]

With the composites wear consists of four components that are wear of the polymer matrix, wear of the fibre, the fibre peel off from the matrix surface and the fibre fracture. [43] With the filled systems when the matrix wears the polymer is lost more readily than the filler and eventually the protruding filler particles support a large fraction of the load and slide over a surface which is lubricated with a thin film of the polymer. The rate of wear is then a strong function of the wear characteristics of the filler. A matrix surface often appears to have an excess concentration of filler and the filler itself suffers appreciable wear or deformation supporting a significant fraction of the load. The counterface is coated with a transferred layer of a type similar to that formed by the polymer itself. In addition the counterface topography is modified by the abrasive action of the filler particles and there is often some evidence of chemical degradation of the sliding members. The transfer layers formed by the composites do adhere more strongly to the counterface and such layer will also maintain a low rate of wear when a plain polymer is slid over its surface. [18]

There is useful literature on the wear behaviour of the short and long fibre reinforced thermosets and the influences of the fibre content and orientation with respect to the sliding direction. The strength of the fibre-matrix interface is a crucial factor governing the wear life of the composite. [26]

3.7 Wear of adhesive joints

With the durability of the adhesive joints the most common concerns seem to be the environmental resistance and the fatigue loads. Fatigue loading is seen in almost all (engineering) structures. A fatigue failure is difficult to predict accurately and can result in a sudden catastrophic failure after years of service. The damage can be initiated or accelerated by the factors such as impact, over loading, corrosion or temperature rise.

Fatigue in the bonded joints is complicated by the multi-component nature of the bonded joints and by the complex stress distributions and material behaviour. The methods of modelling fatigue aim to predict the number of the load cycles until certain event occurs (for example crack initiation or complete failure) or the rate of change of the crack length. In general, the adhesively bonded joints perform very well in fatigue, especially if compared to the mechanically fastened joints. But fatigue combined with difficult environment or with the conditions causing susceptibility to creep may significantly weaken the performance. It is to be noted that with the fatigue testing of the adhesive joints the stress concentrations in the test pieces may be different of those in the real structure (e.g. due to joint geometries or scaling) and thus the actual performance of the joint may not be verified. [14]

The environmental resistance is fundamental to the durability of the bonded joints. On the bonded joints the most common cause of the environmental degradation involves the absorption of the moisture into the joint. The effects are such as plasticisation or hygroscopic expansion of the adhesive or weakening of the interface. The absorbed moisture causes swelling and degradation, which affects the stresses in the joint. The residual stresses arise for example from the changes in temperature which lead to the thermal stresses, from the changes in moisture content which lead to the hygroscopic stresses and from the changes due the chemical reactions which lead to the curing stresses (which in compared to former two are small). [44]

4 DEFINITION OF THE PROTOTYPES

The working environment of the studied polymer-steel hybrid component is aqueous and the operating temperature is typically below 70°C, but can reach up to 80°C. Pressure and high forces, including bending-, impact-, compression-, shear and centrifugal forces may also be present. Therefore the desired characteristics for the polymer part should include resistance to water, good mechanical properties (impact strength, shear strength, fatigue durability), wear resistance (towards abrasive and erosive wear) and strong adhesion to stainless steel. The used steel blades are made of 15/5 precipitation-hardened (PH) steel. If possible the polymer should be usable both as an adhesive between the steel blades and as a matrix around the steel pack. Also fillers or glass fibre may be used if needed.

The hybrid component structures for the testing purposes (Figure 15) were defined by the industrial collaborator. With the model 1 there is only polymer between the steel blades, which means a thick adhesive layer between the steel blades. With the model 2 there is a steel insert between the steel blades, which means a thin adhesive layer between the steel substrates. The overall test component size is 50 mm x 50 mm x 25 mm.

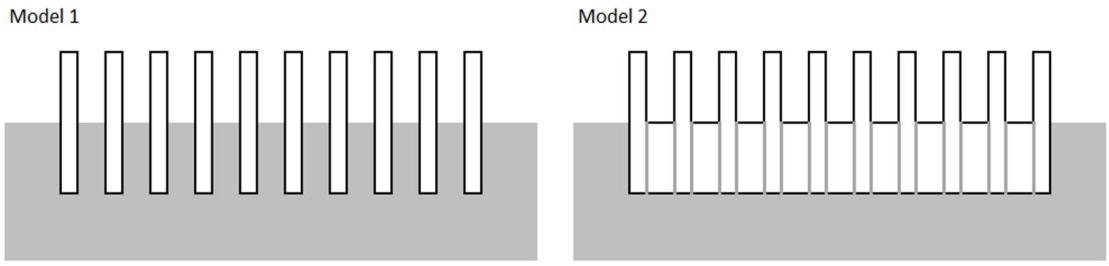

Figure 15 *Cross-sectional structure of the hybrid component, white colour – steel part, grey colour – polymer part)*

5 INDUSTRIALLY APPLICABLE MANUFACTURING METHODS

The manufacturing process to be used for the hybrid component processing depends on the selected hybrid structure and materials. If the thin adhesive (that is the steel inserts between the steel blades) is selected for the hybrid component then a steel blade pack should be prepared first. That means the pre-treated steel blades must first be adhesively bonded together. A special jig may be needed for the pack manufacturing. Also some automated process could be developed for the bonding. The pre-bonded steel blade pack is then added as an insert in a mould before the polymer resin is added. If the thick adhesive (that means there is only polymer between the steel blades) is selected the steel blades could just be pre-treated and embedded in their places inside the mould before the polymer resin (and the reinforcement, if used, as well) is added. The applicable manufacturing methods for the component are shortly described next.

Wet lay-up is the simplest and oldest of the fabrication processes and is a labour intensive and dependent method. The lay-up processes are best suited for the low-volume manufacturing of medium and large sized parts. With the hand lay-up first a gel coat is sprayed onto the mould and then the reinforcing mat or woven roving is placed. Lastly the resin is poured, brushed or sprayed on. Rolling removes the air, densifies the composite and wets the reinforcement. The additional layers are added for thickness. Curing is initiated by a catalyst or accelerator in the resin so hardening may happen without external heating. The spray lay-up is similar to the hand lay-up but offers the greater shape complexity and faster production. A chopped reinforcement and catalysed resin are deposited in the mould from a combination chopper/spray gun. [45]

Vacuum bag processing uses a vacuum to eliminate the air and excess resin from a mould. A non-adhering film is placed over the lay-up and sealed and the vacuum is drawn on the bag. The material is cured at room temperature or with heat. Compared to the hand lay-up this process provides better adhesion between the layers, higher reinforcement concentration and helps to minimise the voids. A pressure bag moulding is similar to the vacuum bag method except the air pressure is applied to a sheet or bag

covering the laid-up to force out the air and excess resin. The pressure enhances the eliminating of voids and increases the density. [45]

Cold press moulding is a press-moulding method using low-pressure cure and inexpensive moulds. A preform or mat reinforcement is placed on a mould and a resin is added. The mould is closed under the moderate pressure. Cold moulding is suitable for the relatively simple shapes. [45]

Compression moulding is a high-pressured process producing the high-strength and complex parts of variety of sizes. A bulk or sheet moulding compound or a preform is placed in the open mould along with the resin. The heated mould halves are closed and the pressure applied. The inserts and attachments can be moulded in. The trimming and finishing costs are minimal. [45]

Resin transfer moulding (RTM) is considered as an intermediate process between the slower spray-up and the faster compression moulding methods and is probably the most widely used of the liquid moulding processes. A reinforcement mat or woven is placed in a mould, which is then closed and clamped. A low viscosity resin displaces the air when it is pumped in under pressure. The material is cured at the elevated temperature under pressure. The moulded-in inserts, fittings and reinforcements can be used. RTM requires higher tooling costs and the moulded part needs trimming. [45]

Injection moulding is a high-volume method enabling very complex parts with the fibres oriented randomly or aligned. Reaction injection moulding (RIM) is a process in which a two-component liquid resin is injected into a closed mould where it reacts and cures. Reinforced reaction injection moulding (RRIM) is similar to RIM, but the short fibres are added to one of the resin components. With the structural reaction injection moulding (SRIM) a fibre preform or reinforcing mat is placed into the mould prior to closure and the resin is injected into a closed mould. Insert injection moulding is a method in which an insert is placed into a mould before the resin is injected into a closed mould. An insert may be any material that can stand the moulding process. [45]

6 ABOUT THE ENVIRONMENTAL FOOTPRINT OF THE HYBRID COMPONENT

The increased environmental awareness and legislation regarding the waste treatment has put the large demands on the material producers (and the end users as well). For example in EU the new directives aim towards the complete responsibility for the product life cycle, from cradle to grave. The waste treatment is even more complicated if the component consists of multiple materials or if the used type of polymer is a thermoset. As the landfilling will be prohibited more widely in the future the new recycling methods need to be developed. The methods for the plastics recycling are for example mechanical material recycling, thermal recovery and chemical recovery. [46]

The recycling processes of the metals are performed at high temperatures and therefore the adhesive/resin used for bonding of the steel blades in the hybrid component would incinerate in the process. Yet with the studied component the polymer part around the hybrid pack could be detached and treated separately. All aforementioned recycling methods are applicable for the thermosets.

Polymers are technically more difficult to recycle than metals and the economic incentives to recycle are less favourable. With the mechanical recycling the crushed material may be used to form a new plastic or it may be used as a filler material. With the thermal recovery heat from the incineration is used to create electricity and/or heat though plenty of ash is left behind. The ashes should be post-treated properly, which means landfilling or recycling. Also the combustion gases need gas cleaning. With the chemical recovery the polymer is chemically dissolved and reused or pyrolysed. In case of the composite material the fibres can be reused too by separating those from the pyrolysis ashes. The possible metal particles can be separated as well.

With the adhesive bonding it should be considered that the used materials, such as the resins, adhesives and the materials and methods used for the surface pre-treatment (for example solvent wipe, chemical cleaning by etching, oxidation and primers) are all chemical products and may contain different substances that are potentially harmful to the human health and environment, though need not to be problematic if treated

properly. Usually these components contain also the volatile components and are flammable and smelly. So the material safety data sheets need to be carefully read and the safety precautions introduced. Depending on the size, the fibres may be harmful too. All scrap and waste from the manufacturing needs to be treated properly and recycled if possible.

On the other hand, if the existing cast steel structure were replaced with the hybrid structure the new lighter component would accomplish the lower power consumption in operation and the better energy efficiency with transportation, and therefore cause less environmental effects.

7 MATERIAL AND MANUFACTURING PROCESS SELECTION

The component which is used in the application currently is made of cast steel. Now it is wanted to be replaced with the hybrid structure consisting of the adhesively bonded steel blades cut from the plate steel. The main objectives are to improve the performance of the product, to lighten the structure and to reduce the amount of machining of the steel blades.

Material selection process has several steps. At first the design requirements are put together in order to outline the required property profile and further the material itself. Then the more detailed product requirements are analysed and a production technology is chosen. Also the costs and environmental issues are analysed before the final decision is reached. At material level the constraints that the material must meet and the objectives that the design must fulfil are first identified. Then the materials are ranked according to which of the material meets the requirements best. [3]

With the adhesive bonding the most important matter is the adhesion between the surfaces. Adhesive systems can be divided into rigid, flexible structural and elastic bonding groups while the sealants form the fourth group. The important mechanical properties are modulus of elasticity, elongation at break and viscoelastic behaviour. Modulus of elasticity governs the stiffness of the joint. The elongation at break is relevant for example for the impact resistance and generally speaking a tougher material may be a safer option. The viscoelastic behaviour determines if creep is expected in the application. All adhesives designed for the each adhesive systems group have quite similar shear modulus (rigid adhesives are often around 1-10 GPa, flexible structural adhesives are in the range of 20 MPa to 1 GPa and the elastic bonding adhesives around 1-10 MPa). The elongation at break is 0-2% with rigid adhesives, 2-150% with flexible structural adhesives and 150-800% with the elastic bonding adhesives. Usually the permanent static load should not be more than 3% of lap shear strength. Depending on the reaction speed, viscosity, yield point and application temperature the adhesives/polymers have different handling properties. [22]

7.1 Polymer material selection

Selecting the best adhesive material for the application can be complicated as there is no universal adhesive to suit all applications. An adhesive system depends for example on the adhesive type, substrate type, surface pre-treatment method and operating environment. Different polymers have different properties such as viscosity (lower viscosity means usually an easier lay-up), curing time (shorter time allows faster production rate), solidification time (shorter time means shorter working time), modulus, stress, stress-strain curve versus elastic-brittle behaviour and impact strength. In general, the adhesives are used under the shear, tensile and mixed loads. With the adhesive joints shear is a preferred load whereas the load in tension or peel should be avoided. Often the joints are exposed to the fatigue stress too.

The properties to be considered in this study are:

- Tensile shear strength
- Adhesion to stainless steel
- Impact resistance, load bearing capability, resistance to fatigue
- Long term durability
- Curing rate
- Heat (and cold) resistance, temperature range
- Water resistance
- Health, safety and environmental issues

One factor yet to be considered is the difference of the coefficient of thermal expansion (CTE) between the joint materials as all materials expand and contract with the temperature changes. With the adhesive bond the most significant changes often occur on cooling. Usually the adhesives have the higher CTEs compared to the metals and those contract more and thus compress the other material causing the residual stresses reducing the strength available transmit the loads. [47]

A bonded structure needs to be durable. High static shear strength in the bonded joint does not necessarily mean good performance under the working environment. For example loading with aqueous environment may lead to a rapid loss of the joint strength. The current cast steel structure of the component is strong and durable; there has not been need to analyse the performance (related to stresses) of the structure as it has been strong and tough enough. Therefore there are no exact strength requirements available either.

The adhesive or resin proposals were asked from the suppliers' technical support. Most of the suggestions included the epoxy adhesives, also polyurethanes were proposed. The chosen materials (see details in appendix 1) for this study were:

- Reichhold's Dion 9102 bisphenol-epoxy vinyl ester resin
- Baule's CG9 9086 82D MF Polyol + B9 M10 MF Iso (hardener) cast polyurethane
- Henkel's Hysol 9466 epoxy adhesive
- Henkel's Macroplast 1351 B25 polyurethane adhesive

7.1.1 Vinyl ester

Vinyl ester resins are resin systems which contain a dimethacrylate monomer and a reactive monomer such as styrene or other vinyl monomer. Most of the properties are gained from the dimethacrylate while the reactive part reduces viscosity, eases the room temperature handling and takes part in the cross-linking reaction. [48]

Vinyl ester is produced by the reaction of an ethylenically unsaturated monocarboxylic acid with an epoxy resin. The most common dimethacrylate monomer is formed in a reaction of methacrylic acid with an epoxy based on bisphenol-A. The other types used are for example epoxy novolac vinyl ester based resin or urethane-based vinyl ester resin. The aromatic rings are in a backbone and impart improved toughness, better strength, higher modulus, higher elongation at break and better heat resistance. The hydroxyl groups aid adhesion and form a reactive site for the structure modification. The unsaturated acid moiety provides the reactive site for crosslinking and gives the curing characteristics. The methyl group increases the environmental resistance for example towards hydrolysis. [48, 49]

The thermal and mechanical properties are similar to those of epoxy resins but have a greater ease of processing. The curing schedule can be tailored to meet the need. The resin cures rapidly due to the reactive vinyl unsaturations at the molecule's ends and enables homopolymerisation/copolymerisation. The secondary hydroxyl groups are able to interact with the hydroxyl groups present on the substrate and thus improve wetting and bonding. The chain growth continues until all unsaturation has been removed or until the vitrification occurs. [48, 49]

Vinyl ester resins are quite brittle and usually require toughening. This may be done by adding a rubbery second phase to the resin. Also the glass beads or the other organic fillers may be used. [48]

7.1.2 Epoxy

Epoxies have been the major adhesives in the structural bonding and have versatile high strength with an excellent performance for example on metals. There are a large number of epoxy resin and hardener combinations. Each of them gives a different cure profile and results in a different molecular structure.

Epoxies are characterised by the epoxide group consisting of an oxygen atom attached to the two carbon atoms which are connected. This epoxy ring is able to react with a variety of substrates which gives the epoxy resins versatility. Epoxies may contain the aliphatic, aromatic or cycloaliphatic backbones. They are prepared from either epichlorohydrin or by direct epoxidation of olefins with peracids. One of the earliest resins is diglycidyl ether of bisphenol-A. The multifuctional aromatic glycidyl ether resins (Novolac resins) and aromatic glycidyl amine resins are also available. They have a high functionality with the increased crosslink density, thermal stability and chemical resistance. Various materials and methods may be utilised to modify the epoxies to improve toughness. [16, 27]

Epoxies have an excellent adhesion to the various substrates, good mechanical properties, good dimensional stability and good resistance to the heat and chemical attack. By combinations of choices of epoxy resin and curing agent the specific needs for the different applications can be formulated. For example for the higher performance applications there are tri- and tetra-functional epoxy resins, which have better mechanical, thermal and water resistance properties. The hardener/curing agent has an important role as it affects the epoxy resin’s handling and performance properties and the curing schedule as well. The commonly used curing agents include amines, polyamides and phenolic resins. A wide range of the available hardeners increases the versatility of the epoxy based polymers. [27]

7.1.3 Polyurethane

Polyurethanes are created by the reaction of a pre-polymer, which contains the reactive isocyanate groups, and a curative (polyol), which contains the hydroxyl or amine groups. The majority of the pre-polymers have aromatic isocyanates such as toluene di-isocyanates (TDI) and methyl di-isocyanates (MDI) as the reactive groups. The aliphatic isocyanates are used occasionally. The curatives can differ, resulting in different physical properties. The pre-polymers are further divided into the polyester and

polyether backbone chemistries, which have an influence on the physical properties. By selecting the type and combination of the isocyanates and polyols the structure can be tailored to obtain the desired properties. The isocyanate affects tensile strength, modulus and hardness while the polyol has bearing on the processing and finished properties. The flexibility to tailor the structure is one of the advantages of the polyurethanes over the other polymers. The urethane groups form strong hydrogen bonds among themselves and with the different substrates. A strong intermolecular bonding makes them useful for the diverse applications. One advantage arises from the high reactivity of the isocyanates. Those are able to react with many substances and form different functional groups. Usually the full properties are developed after a week's curing at room temperature. A further heat treatment may be needed to improve the properties such as toughness or tear strength. [50, 51]

The polyurethane structure is in blocks; in the alternating two different types of segments. The soft segments are derived from the polymeric polyol and the hard segments from the di-isocyanate chain extended with diol or diamine. The different physical forces are present between the segments. The strong secondary bond interactions such as hydrogen bonding between the polar groups of the hard segments are present acting like the reinforcing filler particles. The less extensive interaction forces occur between the non-polar groups of the soft segments. [27, 51]

Polyurethane can interact with the most substrates, such as plastics, wood, metal and glass, through the polar interactions. For example the hydrogen bonds with the polar sites on the urethane and urea groups or the covalent bonds with the substrates having active hydrogen atoms may exist. The relatively low molecular weight and the small molecular size allow polyurethanes to permeate the porous substrates. The isocyanates react with all compounds containing hydrogen atoms attached to a nitrogen atom. In general the isocyanates have a strong affinity to water, which makes them difficult to store. A reaction with water gives an unstable carbamic acid compound which spontaneously decomposes into a primary amine and carbon dioxide together with a subsequent urea group and biuret group formation. [22, 27, 51]

7.2 Preliminary test components

The preliminary test components (see chapter 4) were received from the industrial collaborator. The adhesive/matrix materials used in the first test components were Ashland Derakane TM411-350 (epoxy vinyl ester resin based on bisphenol A epoxy resin) with the hardener Akzo Nobel Butanox M50 1,5% (methyl ethyl ketone peroxide in dimethyl phthalate) and Reichhold Dion 9102 (bisphenol-epoxy vinyl ester resin) with the hardener Reichhold Norpol Peroxide 24 2% (cumene hydroperoxide).

Glass fibre was used as a resin reinforcement material. Both continuous/long and discontinuous/short fibres were used in a form of mat, roving yarn or randomly oriented chopped roving. The fibre volume content/fraction was around 50 weight percent. The 15/5 PH steel pieces/blades were laser cut from the larger steel plate.

The test components were manufactured by hand in a wet lay-up process. A three-piece metallic mould was used. For the mould pre-treatment bees' wax was used. The steel blades, which were wiped with ethanol, were laid side by side (with a gap for the polymer resin in between) in upright position in the bottom of the mould. Then the fibres, which first were cut into fitted size, were added into the mould and impregnated with resin. The top-piece of the mould had the escape grooves for the excess resin. The mould was then closed, pressed and cured. The function of the middle piece of the mould was to ease the cured part removal. One of the test pieces was vacuum moulded, but the end result did not convince even visually.

7.3 Surface treatment

With the adhesive bonding the surface of the substrate must first be cleaned and degreased of contaminants with a detergent or solvent. For the stainless steel one choice is for example acetone. As a cleaning method wiping or ultrasonic cleaning are usually adequate. [27, 47] The ultrasonic cleaning takes place when the high frequency bursts of ultrasonic energy are applied to liquid cleaning solution that surrounds the parts. The alternating waves create bubbles which implode creating a micro-jet action that penetrates and cleans the surface.

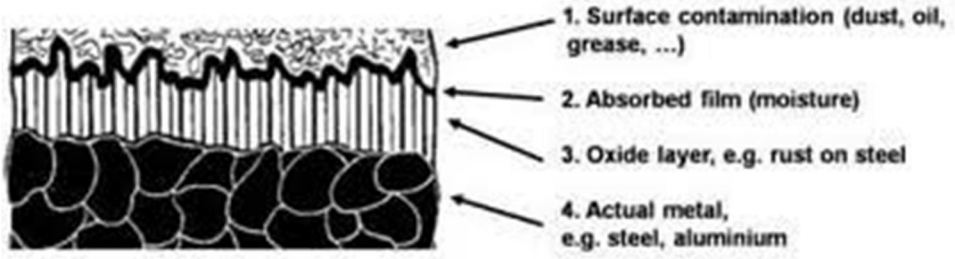

***Figure 16**: Typical surface layers of a metal substrate [52]*

To enhance the adhesion mechanical abrasion such as sanding or abrasive blasting, which change the substrate profile, may be enough. With blasting the level of abrasion is important as an excessive abrasion causes folding of the surface and may lead to trapped moisture, which then may evaporate during curing and cause voiding. Thus the abrasive blasting should be light enough to avoid folding, but heavy enough to remove for example the surface oxides. Sometimes more complex treatment may be necessary; for example a chemical treatment such as nitric and phosphoric acid etching, anodizing in nitric acid or plasma treatment can be used. Thus no general etching or anodizing treatment exists to provide the superior bond durability in moist environment due the iron oxides on the steel surface. Mechanical interlocking may often be needed alongside the chemical bonding in order to achieve moisture resistance. [2, 22, 27, 47]

Deposited coating, such as conversion coating or thermal spray, may provide more corrosion resistant surface by stabilizing the surface from degradation and by forming physical bonds with the adhesive or primer. An adhesion promoter improves the bond strength between the adhesive and substrate. The coupling agents or primers, such as silane and titanate, are used to enhance the durability of the bonded steel structures. [47] The silanes have become widely accepted primers to prevent degradation of the bonded joint. They contain the hydrophilic and hydrophobic moieties and act as a coupling system between the organic adhesive and inorganic metal surface. Each adhesive system requires a distinctive silane and the silanization parameters such as concentration, temperature and surface pre-treatment have influence on the joint. A sol-gel process which provides a graded interphase between the metal and adhesive can be used as well. This primer, which forms covalent bonds between the substrates, consists of an inorganic component that concentrates at the metal surface and an organic component and sometimes a coupling agent which concentrate at the adhesive. [27] If the surface needs to be protected until prior to bonding a peel ply may be added [47].

7.4 Further considerations

As the aqueous environment with the elevated temperature is present in the operating environment and the humid aging is one of the main causes of the polymers long term failures the corresponding ageing should be regarded in this study.

In case the thin adhesive structure (that is the steel inserts between the steel blades) is chosen a constant bond line thickness needs to be formed and guaranteed during the steel pack adhesion process. It also needs to be decided how much pressure (max/min) is applied to a bond during the preparation and curing processes as the pressure prevents adherents to move or be separated. Pressure also forces the polymer to penetrate into the substrate surface. Squeezing of the bond must be avoided not to remove the adhesive from the joint. For example spacing aids such as beads, wires or foil may be utilised.

The operating and curing temperatures need to be defined as well. Among the other things, such as the material properties and processing time, it sets the residual stresses within the operating temperature. For example the coefficients of thermal expansion, α, are different between the polymer and steel, the CTEs of the polymers usually are 10-100 times those of the other materials [27]; α for the vinyl ester resin is $15\text{-}100 \times 10^{-6} K^{-1}$, for the epoxy $20\text{-}150 \times 10^{-6} K^{-1}$ and for the cast polyurethane $50\text{-}200 \times 10^{-6} K^{-1}$ while for the steel it is $11 \times 10^{-6} K^{-1}$.

8 TESTING

The interests of the product performance are the short- and long-term responses of the loaded component. For the short-term there are for example the tensile- and impact tests. For the long-term the responses depend on the properties measured using the techniques such as the stress relaxation test and the creep test. [6] The dynamic mechanical thermal analysis (DMTA) is an excellent technique for extracting information on dynamic material properties which relate to viscous and elastic behaviours [25]. The strength of an adhesive joint depends on the stresses formed in the loaded joint. The typical forces to the adhesive bonds are the tensile, shear, peel, cleavage and compressive forces (Figure 17).

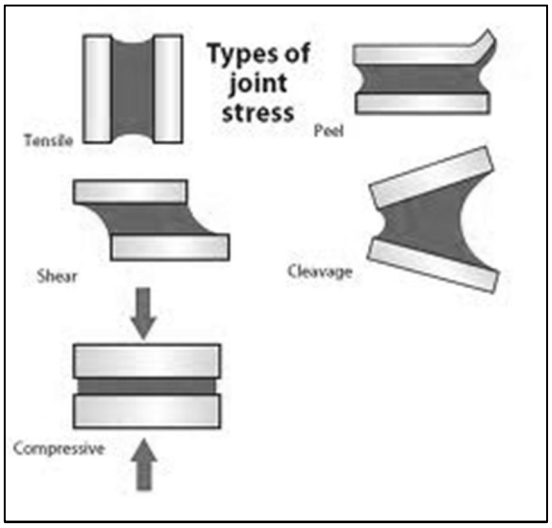

***Figure 17**: Types of joint stress [53]*

The fracture toughness of the component is one of the interests. It may be tested with the tests such as the double cantilever beam (DCB), notched flexure and cracked lap shear. The DCB test method covers the determination of the fracture strength in cleavage when tested on standard specimens under the specified conditions. [54]

For the adhesives a tensile shear resistance test is one of the most important tests because the adhesive bond shows a good resistance to tensile shear stresses and it is always recommended to load the bonded parts in the tensile shear mode in order to get the highest resistance. The mode of rupture, which may be adhesive, cohesive or mixed,

should also be carefully noted [22]. It should be kept in mind that if a lap shear test is undertaken shortly after completion of the bonding the acceptable lap shear strengths may be obtained. However, the long-term bond strength depends on the resistance to degradation over time and the bond may fail despite this accepted test. [2]

The wedge or cleavage test is used to evaluate the adhesion of the rigid substrates. Cleavage arises when a tensile force is unevenly applied to the one edge of the joint, forcing it to open. This kind of stress is bad for the adhesives as the adhesive bonds do not have so good resistance to cleavage. [22] Often this test is used for the observation of the crack propagation rates through the adhesive [17]. The wedge cracks the adhesive leaving the chemical bonds in the joint just ahead of the crack under a very high tensile stress which worsens the effects of the hydration. Any surface which is not resistant to the hydration usually causes the joint to fail interfacially. By measuring the rate of the crack propagation over a reasonable period of time, a comparative measure of durability can be obtained. The wedge test is a comparative test only and does not produce design data. [23]

As the higher peel strength adhesives are continuously developed the test methods needs to be developed as well. A peel test has become a part of the adhesive performance testing. The peel resistance is the average force required to separate the adhesively bonded adherends. The T- (or 180°) and 90° peel tests are widely used. [22]

When bonding the structural and rigid materials such as metals and composites, it is important to know how the bond will resist the various impacts. The impact test methods are used to evaluate the materials capability to withstand the high velocity impact loadings. Temperature influences also to the impact resistance. [6, 25]

A standard result review for the wear test, as defined by the ASTM International and respective committees, should be expressed as a loss of material during wear in terms of volume. The volume loss gives a truer picture than the weight loss, particularly when comparing the wear resistance properties of materials with the large differences in density. The standard test methods are available for the different types of wear. It should be noted that the test methods have inbuilt limitations and do not give a true picture in every aspect. The standard wear tests should only be used for the comparative material ranking of a specific test parameter as defined in the test method. For the more realistic values of the material behaviour in the real applications it is necessary to conduct wear testing under the conditions simulating the exact wear process. [54]

The most important tribological property is the wear rate. The inverse of the wear rate is usually referred to as the wear resistance of a material. The choice of the type of the wear test configuration must be based on the tribotechnical system under consideration. The latter determines the elements of the basic structure of the tribosystem which yields information on the existing wear mechanisms and the loss of material. Therefore the tribological testing of the materials under laboratory test configurations can only be considered as a helpful screening tool. The final choice of the right material combination is always dependent on the results of the subsequent field tests by the use of the real structural components. [5] The mechanisms and environments are different when a small-scale and a large-scale behaviour and the application limits are evaluated. For example the wear behaviour of the test samples with small and large contact areas is significantly different for the solid lubricated composites, with the lower specific wear results for the large-scale samples. Transitions in lubrication mechanism due to softening and melting do not allow for extrapolation and justifies the use of the large-scale tests. [35]

8.1 Test methods related to adhesives and wear

A table of the standard methods mentioned in this chapter is found in the appendix 2.

The standard tests such as ISO 527, DIN EN ISO 604:2003-12 and ASTM D638 are available to evaluate the stress-strain behaviour of the polymeric materials. For the creep test the standards like ISO 899 or ASTM D2990 can be used. The standard procedures for the dynamic mechanic testing are described in ISO 6721-2:2008 and ASTM D4065. With the fibre-reinforced polymer composite the compression strength after impact may be determined by the standard tests ASTM D7136 (impact damage resistance) and ASTM D7137 (compressive residual strength after impact). [6, 54]

Temperature sets limits for the polymer usage as the polymers soften under heat. What the limiting temperatures are at which a polymer component can still be loaded with the moderate deformations can be tested with the standard tests like the Vicat temperature test (ISO 306 and ASTM D648), the Martens temperature test (DIN 53462:1987-01) and the heat-distortion temperature test (ASTM E2092-09). [6, 54]

A measurement of the adhesion between the two surfaces is often performed by a tensile test of a lap shear specimen. The standards for the lap shear test are for example ISO 4587, ASTM D1002, ASTM D3528 (-78 for double lap shear, -96 for double strap

shear) and DIN EN 1465:2009 (Figures 18 and 19). A thick adherend test is specified in the standards ISO 11003-2 and ASTM D5656. This method may be used to determine for example the shear properties of an adhesive, a shear modulus of an adhesive or the effects of temperature, environment or testing speed.

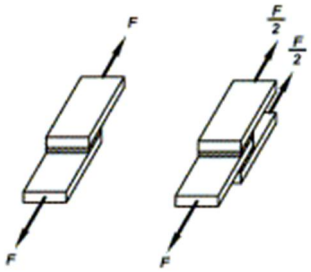

Figure 18 *Single and double lap shear test specimen. Adopted from [55]*

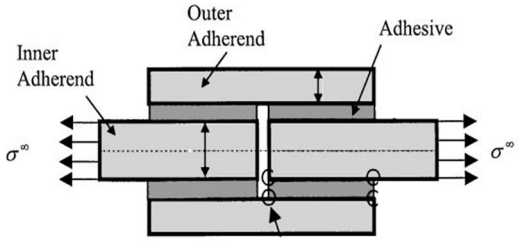

Figure 19 *Double strap shear test specimen. Adopted from [56]*

The stress state that exists in the specimen during testing is complex as the ends of the bond are under combined tensile and shear loading. The adhesives are best used in shear where they can withstand much larger forces than in tension. [17, 22] During the single lap test the joint rotates as it is loaded which results in the substrate loads that vary non-linearly with the applied joint loading (Figure 20). In the double lap joint the centre substrate experiences no rotation. The substrates deform in tension whilst the adhesive deforms in shear. So the failure mode alters from peel to shear. If tapering is used it minimises the peel stresses further and increases the bond strength. [47]

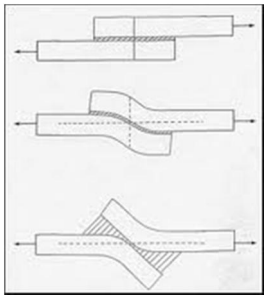

Figure 20 *Rotation of single lap joint specimen. Adopted from [57]*

In the wedge test, for example the standards ISO 10354 and ASTM D3762, the specimens are wedged apart (Figure 21) and the crack propagation is followed. It tests

the durability of the fractured and stressed adhesive joint. The test environment is variable and may for example be hot and wet. [23] The impact wedge peel test, ISO 11343, specifies a dynamic impact wedge method for the determination of the cleavage resistance under the impact loading of the high-strength adhesive bonds between two metallic adherends.

Figure 21 *Wedge test specimen. Adopted from [58]*

The DCB test is used to find out the mode I fracture energy. The standard methods for the test are for example ASTM D3433 and ISO 15024:2001. First a crack is initiated with a wedge. Then the two beams of the specimen are pulled apart (Figure 22). As the load increases to the critical load the crack starts to propagate and the pulling is stopped. The deflection of the beams is kept constant and the load drop and the crack length are measured.

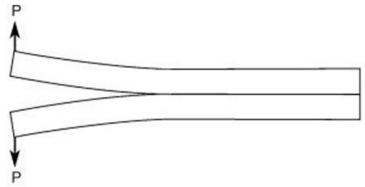

Figure 22 *Double cantilever beam specimen. Adopted from [59]*

A peel test, described in the standards such as ISO 8510-2, ISO 11339, ASTM D1876, ASTM D1781-76 and ASTM D3167, is a test that measures the peeling of an adhesive joint. That is the strength required to pull apart the bonded surface (Figure 23). The test can be performed as 90°, 180° or arbitrary-angle peel test. [22]

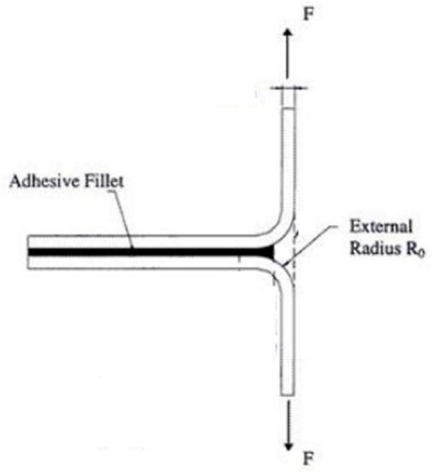

Figure 23 *T-peel test specimen. Adopted from [60]*

The standard test methods for the shear impact strength of the adhesive bond are ISO 9653 and ASTM D950. The tests measure the energy absorbed by a specimen when the adhesive bond between two blocks (a smaller block is adhered to a larger block fixed to base) of the adherend is sheared by a single blow of the test machine hammer. At impact the joint is subjected to a high rate shear loading and is fractured. [47] The pendulum testers are available not only the blocks but also for the other shapes such as lap joints [47, 54]. An Izod test evaluates the impact resistance of a cantilevered notched bending specimen as it is struck by a swinging hammer. For the Izod test the standard methods are ISO 180 and ASTM D256. A Charpy test evaluates the bending impact strength of a small notched or un-notched specimen that is stuck by a hammer. The Charpy test is described in the standards ISO 179 and ASTM D256. In addition the impact test sometimes brings out a brittle failure in materials that undergo a ductile breakage in a short-term tensile test. A falling dart test (described in the ASTM D5420 and D5628 standards) suits for the specimens that are too thin or flexible to be tested with the Charpy or Izod tests. It also works well when the fracture toughness of a finished product with the large surfaces is sought. [6, 25]

The standard fatigue tests are for example ISO 9664 and ASTM D3166 tests. In the latter ASTM test a cantilever beam is held in a vice and bent at the other end by a yoke, which is attached to a rotating variably eccentric shaft. A constant stress throughout the test region in the specimen is achieved by its triangular shape. The fatigue test results are plotted as stress amplitude versus number of cycles to failure (S-N curves). [6,25] These standard tests are usable for the fatigue strength of the bond too and they test the fatigue properties of the adhesive in shear by tension loading. [54]

The measurement of the adhesion between the fibres and matrix is much more difficult. The example testing methods are the fibre pull-out test and short-beam fragmentation test. [17]

The standard tests are used to characterize the tribological behaviour of the polymer materials in the laboratory. The types of the test configurations chosen for the evaluation of the materials are for example pin-on-disc test and block-on-ring test (Figures 24 and 25). The standards ASTM G77 and ASTM G99 or ASTM G176 may be utilised. [7, 54]

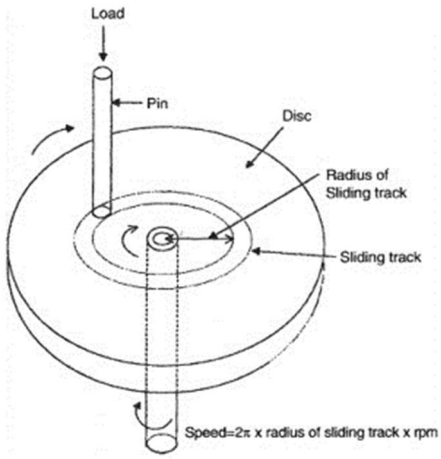

Figure 24 *Pin-on-disc test. Adopted from [61]*

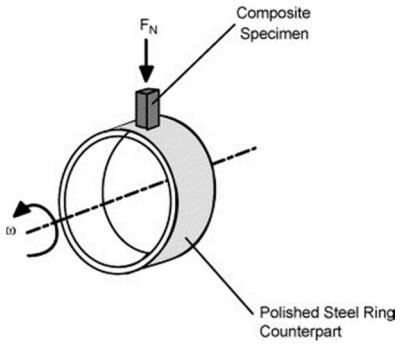

Figure 25 *Block-on-ring test. Adopted from [62]*

Abrasive wear can be measured as loss of mass by the Taber Abrasion Test according to ISO 9352 or ASTM D1044 [54]. The fretting tests are conducted with a group of unfilled polymers paired against a steel ball. The area of the fretted scars on the specimen can be measured with an optical microscope, scanning electron microscopy, electron probe microanalysis or ferrography. [41]

8.2 Test procedures used

In this section the used test procedures and arrangements are introduced. Also further test methods related thoughts are provided.

8.2.1 Bending and water absorption test

The first test components were numbered as 1.1, 1.2….8.2 where x.1 and x.2 indicate the structure: 1 – plain (thick) polymer between the steel blades, 2 – a steel insert and (thin) polymer between the steel blades (see chapter 4). The components 1.y-4.y were of Derakane TM411-350 vinyl ester and the components 5.y-8.y of Dion 9102 vinyl ester.

The bending test of one steel blade was done for these first test components (see section 7.1.5). The test was performed to study how the preliminary component withstands load when one of the steel blades of the hybrid structure is bent (Figure 26). The tested components were numbered as 4.1, 4.2, 7.1 and 7.2. At first the components were tested while being at room temperature and normal RH. The second test (for the different blade) was carried out after the components were exposed to hot water (80°C) for nine days. The tests were done with a standard tensile testing machine (Instron 5967) with 30 kN load cell and with a special jig/clamp.

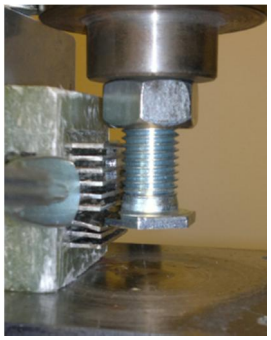

Figure 26 *Bending of the steel blade of the hybrid component*

8.2.2 Lap shear test

The lap shear test was performed to analyse the effects of the surface pre-treatment, polymer type, bond thickness and environmental effect to the bond strength. The results of the lap shear tests are presented in terms of the load versus the displacement/extension. The maximum shear strength, the shear stresses, the extension at maximum load and at failure and the type of the failure were analysed from the test results.

For the bond strength characterisation the modified ASTM D3528 (Type B specimen) test was used (Figure 19). It is a double strap test and useful for the determination of the shear stress values as it makes a conversion of direct tension to lap shear. The chosen specimen sizes were: the longer steel part 25 mm wide, 100 mm long, 1 mm thick and the shorter steel part (strap) 25 mm wide, 50 mm long, 1 mm thick. Thus the strap length was 50 mm (that is 25 mm overlap of the shorter steel part with the longer one). Five replicates per each test combination (see appendix 3) were prepared and measured.

Prior to bonding the steel adherends were pre-treated. Two different pre-treatment methods were used: alternate 1 was degreasing (ultrasonic clean with acetone) and alternate 2 was degreasing (ultrasonic clean with acetone), glass blasting and second ultrasonic clean with acetone. The other, more effective pre-treatment options were considered as well, but were left out from this thesis. After the pre-treatment the surfaces were rinsed with deionized water and ethanol.

The adhesives were mixed according to the manufacturers' recommendations and spread with the spatulas on the steel surfaces. Two steel plates were butted and bonded together with a double strap joint. The joint was formed in two phases, one strap side at a time. A uniform bond thickness was controlled with either 0.1 mm metal foil or with 1 mm steel plate. A special fixture/jig was used to ensure the correct placement of the parts (Figure 27). Pressure on the joint was gained with the weights (226-229 g) at the specimen ends.

Figure 27 *The specimens and weights in a fixture/jig used for preparation*

The curing times for the specimens were according to the manufacturer's recommendations at 23°C. The post curing time was 7 days and temperature 23°C. The

accelerated ageing was carried out for the half (60) of the samples after the post curing: the adhesive joints were immersed in 80°C water for 7 days.

The tests were conducted with the standard tensile testing machine (Figure 28). The specimen A1-4, A36-40, C1-10, C21-40, D1-5, D21-25, D36-40 were tested with Instron 8801 with 100 kN load cell. The specimen A5-10, A21-35, B1-10, B21-40, D6-10, D26-35 and DX1-2 were tested with Instron 5967 with 30 kN load cell. The crosshead speed was 2 mm/min until failure. The series of tests were carried out on the specimens bonded with the adhesive alternatives under the laboratory conditions (23°C, ambient/normal RH). The aged specimens were tested directly from the hot water bath. Five samples of each four adhesive per each variable combination (bond thickness, steel pre-treatment, with or without ageing) were tested, which was 120 tests all together.

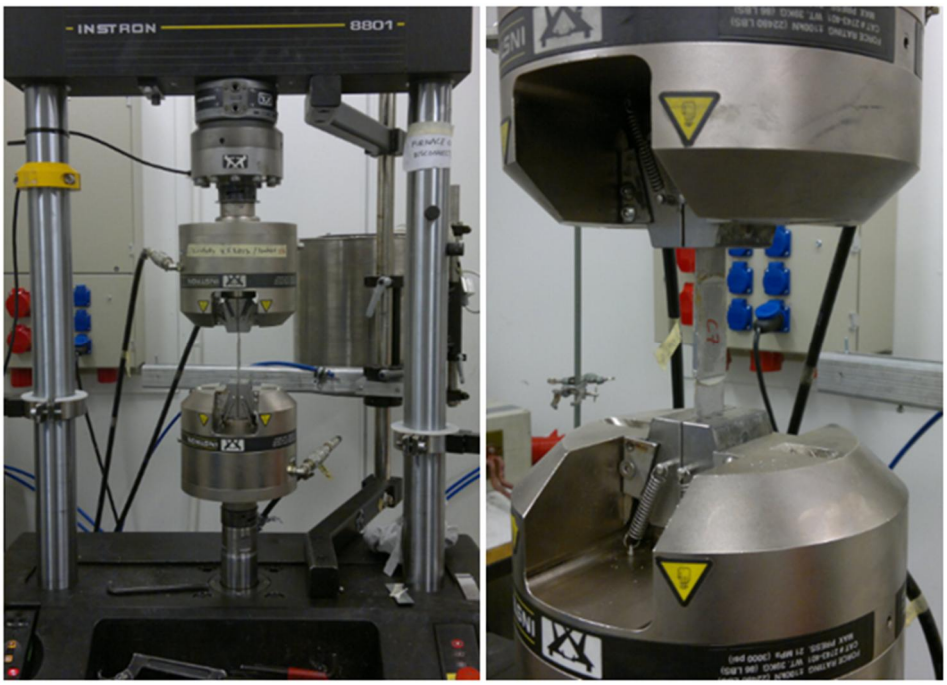

Figure 28 *Instron 8801 tension test equipment setup*

8.3 Thoughts for the further testing

Preliminary some the following tests were planned to be done during this thesis work. But due the lap shear test results these were decided to be left out at the moment as more analyses of the adhesive materials and the joint variables needs to be done before prototyping and testing the actual hybrid structure.

Fatigue test could be done for the selected polymer materials. The similar test specimens that were used with the double strap shear tests may be utilized. Preferably the tests should be conducted in humid environment.

Modified pin-on-disk test could be used to test the wear properties and the durability of the hybrid component to see how the component withstands wear. The effect of the pin-on-disk test on the structure properties may then be studied with the further tests that are compression-, bending- and tensile strength test (see the following text). In the pin-on-disk test the hybrid component itself acts as the pin of the test. A special jig is needed to strap the component. Predetermined pressure is applied to the pin and a rotating turntable with applied load causes sliding wear and friction force (result in shear, bend, fatigue) on the component. The controlled tester values are such as vertical load, contact stress and turntable speed.

Bending test of one steel blade of the hybrid component (Figure 29) could be performed after the pin-on-disk test. With this test is measured how the component withstands the bending moment. The test may be done with the standard tensile testing equipment (Instron 5967) with a special jig and clamp.

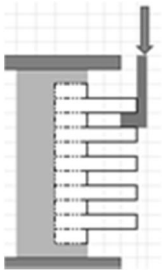

Figure 29 *Blade bending test sketch*

The first tensile strength test (Figure 30) could be performed directly after the pin-on-disk test run and the second test after the bending test. With this tensile test the steel blade adhesion strength to the adhesive/hybrid structure may be analysed. The test may be done with the standard tensile testing equipment (Instron 5967) with a special jig and clamp. For this test the tested steel blades must be notched to attach them to the pulling jig. Preferably notching is done before the component is prepared.

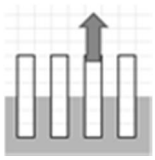

Figure 30 *Blade tensile test sketch*

During this thesis the properties, which were supposed to be the most important (that are adhesion and strength) to this application were planned to be analysed. For the

further studies the following test methods may be useful in order to find out more relevant properties for the adhesive and/or the structure.

A wedge test is ideal to evaluate the bond durability because with the test the bond is placed under the most aggressive stress (tension at near the adhesive material ultimate tensile strength) while being exposed to conditions which promote hydration. The stress applied at the crack front diminishes as the crack length increases. [14] The standard procedures are ISO 10354 and ASTM D 3762. Another test to evaluate the fracture strength is the DCB test, which is for the fracture toughness determination. The standards for the test are ASTM 3433 and ISO 15024:2001. One standard procedure describing the determination of the strength of the adhesive joints is ISO 15108: 1998. This method may be used for comparing materials.

The compression test of the whole hybrid component (Figure 31) could also be performed (directly) after the pin-on-disk test. This test could be used to study how the component withstands compression and how it affects the component's properties. For example it may alter the bending or tensile test (see section 8.3) results. The test may be done with the standard compression testing machine.

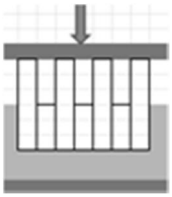

Figure 31 *Hybrid component compression test sketch*

9 RESULTS AND DISCUSSION

The results obtained from the bending and double strap shear tests are presented and discussed in this chapter (and also in appendixes 4 and 5); the hybrid component results in the section 9.1 and the double strap shear test results in the sections 9.2-9.6.

The following abbreviations/terms are used for the tested materials and variables. The hybrid components numbered as 4.1-4.2 are of Derakane TM411-350 vinyl ester and the components 7.1-7.2 of Dion 9102 vinyl ester and x.1 means plain polymer between the steel blades and x.2 a steel insert and polymer between the steel blades. With the double strap shear tests the specimens A are of Dion 9102 vinyl ester resin, B of Baule CG9 9086 82D MF + B9 M10 MF cast polyurethane, C of Hysol 9466 epoxy adhesive, D of Macroplast 1351 B25 polyurethane adhesive. The specimen numbers indicate the test variable: 1-5 (acetone wiped steel and thin bond), 21-25 (glass blasted steel and thin bond) and 31-35 (glass blasted steel and thick bond). Aforesaid specimens were post cured at 23°C and normal RH for one week. The hot water exposure at 80°C for one week was done for the specimens numbered as 6-10 (acetone wiped steel and thin bond), 26-30 (glass blasted steel and thin bond) and 36-40 (glass blasted steel and thick bond).

9.1 Hybrid component related tests

Water intake of the hybrid component was measured during the hot water exposure (Figure 32). The percentage values of the total weight change were calculated:

$$\frac{w(t)-w(0)}{w(0)} * 100\% \ , \qquad (9.1)$$

where w(0) - component weight at the start and w(t) – component weight at the end.

The size of the polymer part of the specimen was (width x depth x height) 50 mm x 50 mm x 17 mm. The steel blade size was 30 mm x 1 mm x 16 mm and the steel insert size was 30 mm x 2 mm x 8 mm. The steel blades were half (8 mm) embedded in the polymer.

During the hot water exposure the Derakane specimens (4.1-4.2) absorbed 43% more water when compared to the water absorption of the Dion specimens (7.1-7.2). The

individual percentage weight gains of the specimen were 4.1: 0,52%, 4.2: 0,22%, 7.1: 0,36% and 7.2: 0,15%.

In bending test the steel blades of the hybrid component bent elastically and no remarkable deformation occurred in the polymer. In general, the test did not provide much results (see appendix 4) as no failure point of the structure (or the bonding failure between the steel and polymer) could be analysed from the curves. Hence more suitable test method needs to be found/applied. Anyhow the results showed different behaviour between the specimen with the steel insert between the steel blades and with the specimen plain polymer between the steel blades. The hot water exposed specimen gained higher stress values than the dry specimen when there was a steel insert between the steel blades. With plain polymer between the steel blades the results were converse. In general a stronger structure was gained with the steel inserts, which was also expected.

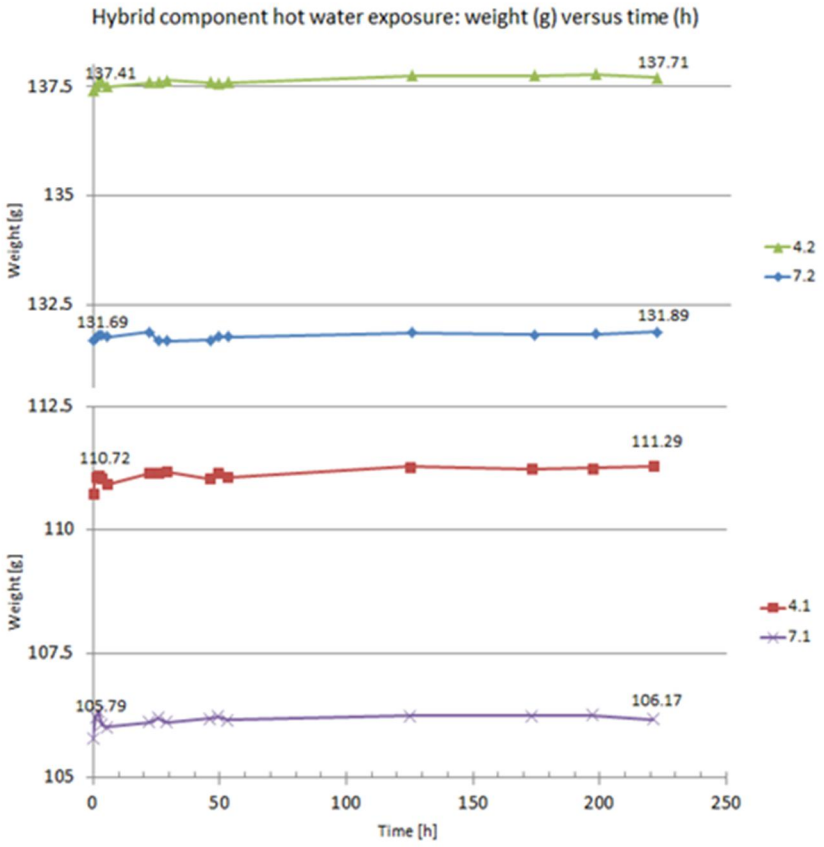

Figure 32 *Weight gain of the hybrid component during the hot water exposure*

9.2 Water intake of double strap specimen

Water intake of each double strap specimen was followed by measuring the specimen weight before and after the hot water exposure (Figure 33). The percentage values of the weight change per each specimen were calculated:

$$\frac{w(t)-w(0)}{w(0)} * 100\,, \tag{9.2}$$

where w(0) - weight at the start and w(t) – weight at the end.

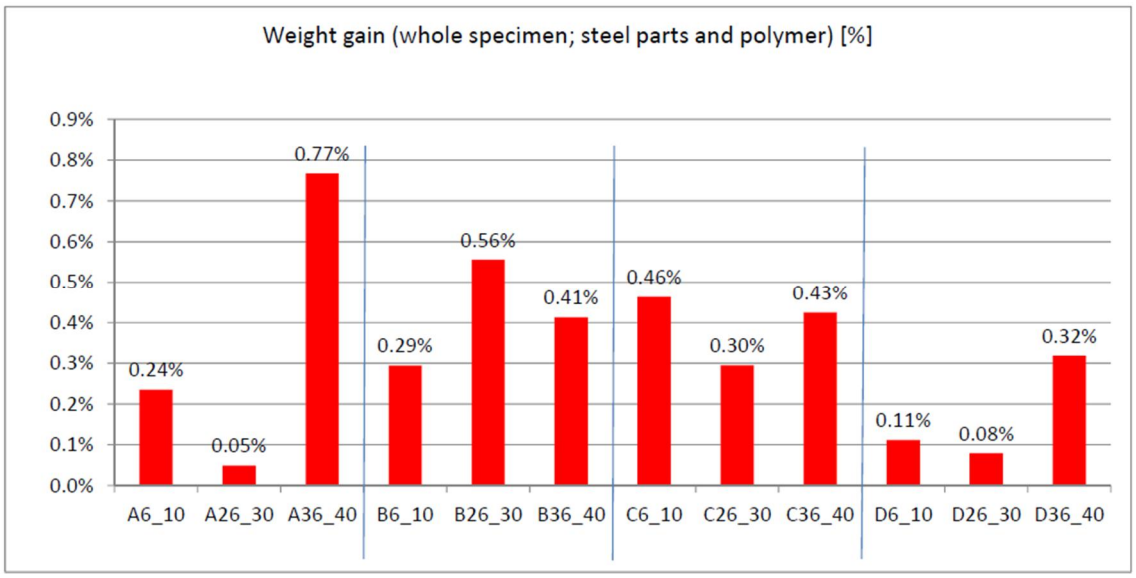

Figure 33 *Double strap specimen's weight gain during the hot water exposure*

According to the results no equal type of behaviour can be seen among these different polymers though B differed most from the others. The steel surface's glass blasting treatment with the thin bond redused the water intake (except with B in which the increase was 89%) when compared to the acetone wiped steel; with A the reduction was 79%, with C 36% and with D 29%. Increasing of the bond thickness increased the water intake (except with B in which the reduction was 26%) when compared to the glass blasted thin bond; with A the increase was 1477%, with C 44% and with D 303%. After the specimens were broken pure water could be seen on the surfaces of the specimen A6-10, A36-40 and D36-40.

9.3 Shear stress

The lap shear stresses were calculated from the double strap shear test results by dividing load by the bond area:

$$\tau = \frac{F}{2*b*L} \quad , \tag{9.3}$$

where τ – shear strength, F – force, b – bond width, L – bond length

With the Dion thin bond line result curves (Figure 34) can be seen that the best results are with the dry glass blasted steel specimen. The hot water exposure degraded the results; the worst results were gained with the acetone wiped steel specimen but the glass blasted steel did not made much better. The different slope of the curve with the acetone wiped steel specimen (A1-4) may be explained by the usage of Instron 8801 test equipment for testing these specimens. Instron 8801 is heavier equipment with 100 kN load cell and thus may cause a smaller equipment dependent strain than Instron 5967 with 30 kN load cell. Therefore the slope may be steeper as well.

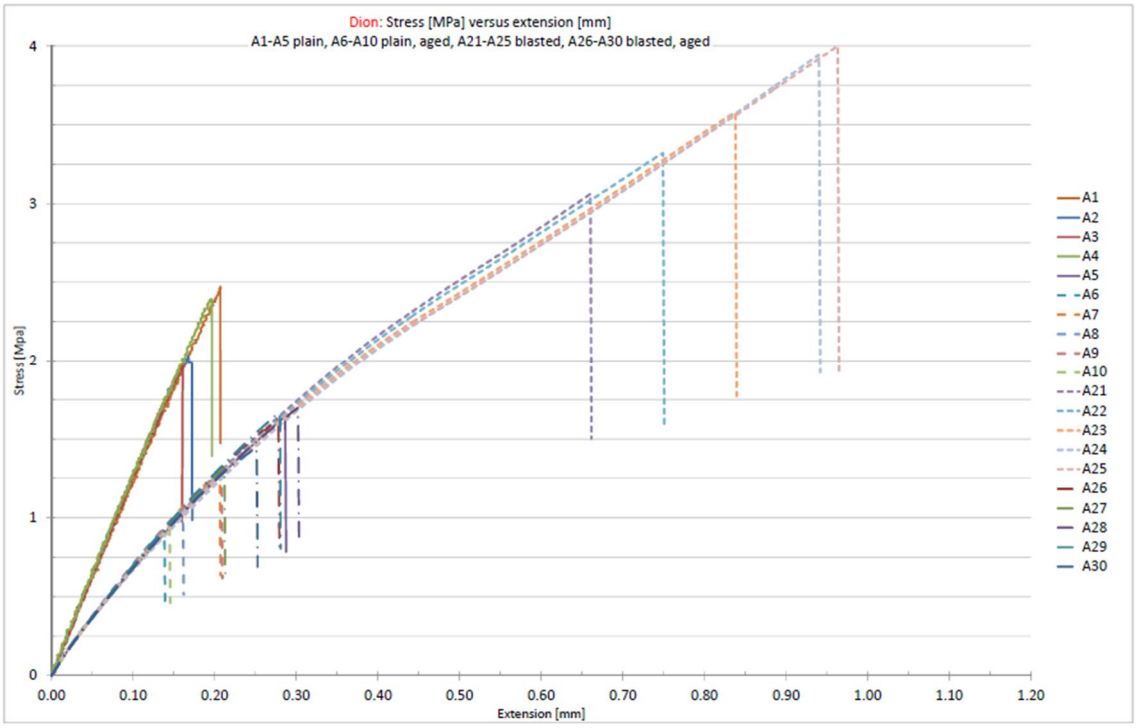

Figure 34 *Double strap shear stress curves of Dion vinyl ester resin with thin plain (A1-10) and with thin glass blasted (A21-30) steel bond*

When compared the Dion glass blasted steel specimen with and without the hot water exposure (Figure 35) the dry thick bond specimen gained the best results though the dry thin bond option was not much weaker. Again the hot water exposure degraded the results; the worst results were gained with the thick bond specimen and the thin bond

specimens were only a bit better. The different slope of the curve with specimen A36-A40 compared to the others may again be explained by the usage of Instron 8801 testing equipment for the measuring of these specimens.

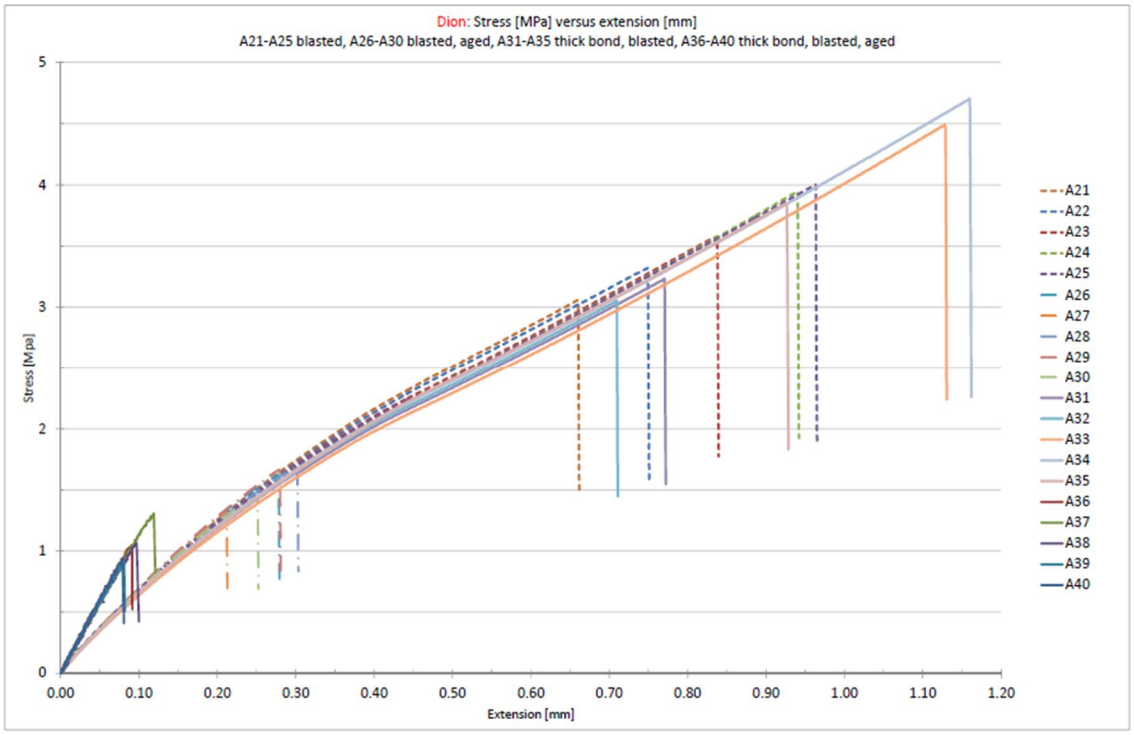

Figure 35 *Double strap shear stress curves of Dion vinyl ester resin with thin (A21-30) and with thick (A31-40) glass blasted steel bond*

As with Dion also the Baule results (Figure 36) show that the best results are with the dry glass blasted steel specimen. With the specimen B21 and B24 the bonds were so strong and/or ductile/tough that the steel part broke instead of the joint. The hot water exposure substantially degraded the results. It also seemed to make the polymer quite sticky. The worst results were gained with the hot water exposed glass blasted steel specimen and the acetone wiped steel was almost equally weak.

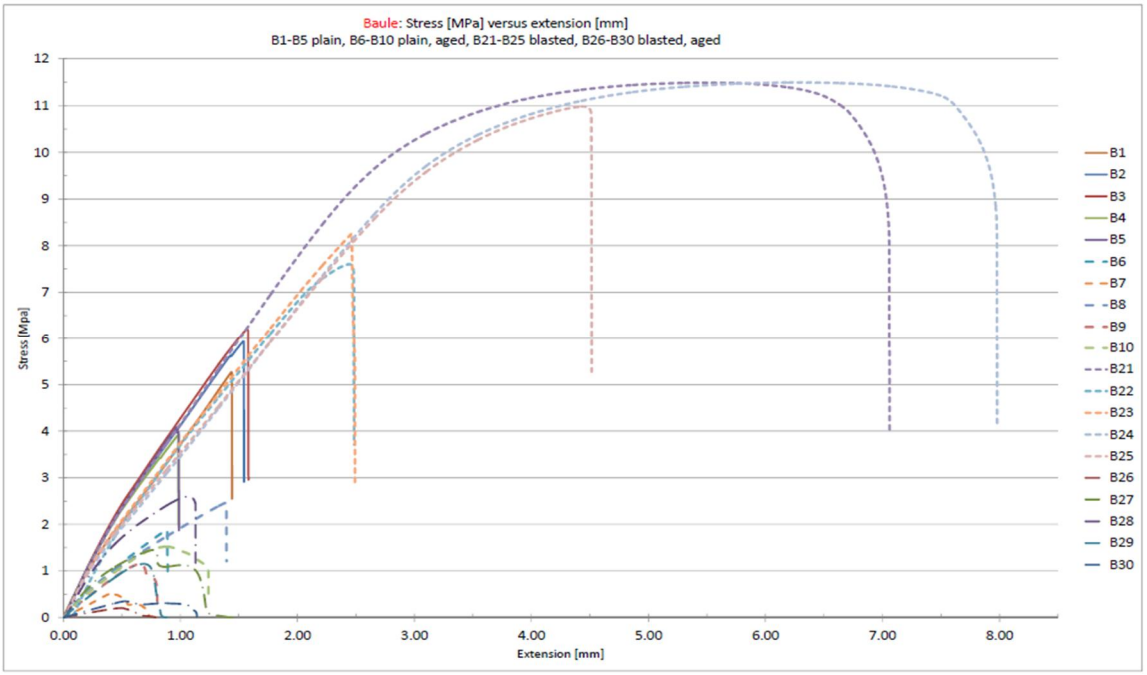

Figure 36 *Double strap shear stress curves of Baule cast polyurethane with thin plain (B1-10) and with thin glass blasted (B21-30) steel bond*

When compared the Baule glass blasted steel specimen with and without hot water exposure (Figure 37) the dry thin bond specimen gained the best results, also thick dry bond made quite well. The hot water exposure significantly degraded the results; the specimens with the thin bond had the worst results, and the thick bond results were little better and more ductile.

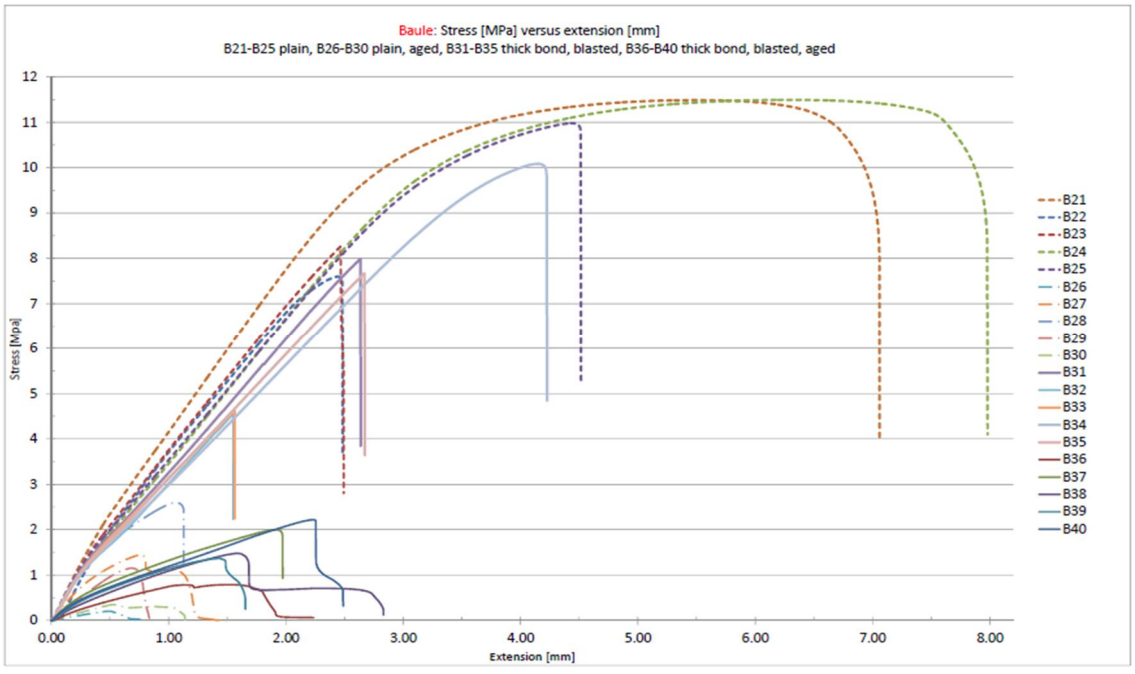

Figure 37 *Double strap shear stress curves of Baule cast polyurethane with thin (B21-30) and with thick (B31-40) glass blasted steel bond*

Also with Hysol (Figure 38) the best results are with the dry glass blasted steel specimen. With the specimen C23 and C25 the bonds were so strong and/or ductile/tough that the steel part broke instead of the joint. Once again the hot water exposure substantially degraded the results. The worst results were gained with the glass blasted steel specimen. To be noted that all Hysol specimen were measured with Instron 8801 thus the result curves possibly are therefore steeper that they would be if Instron 5967 had been used instead.

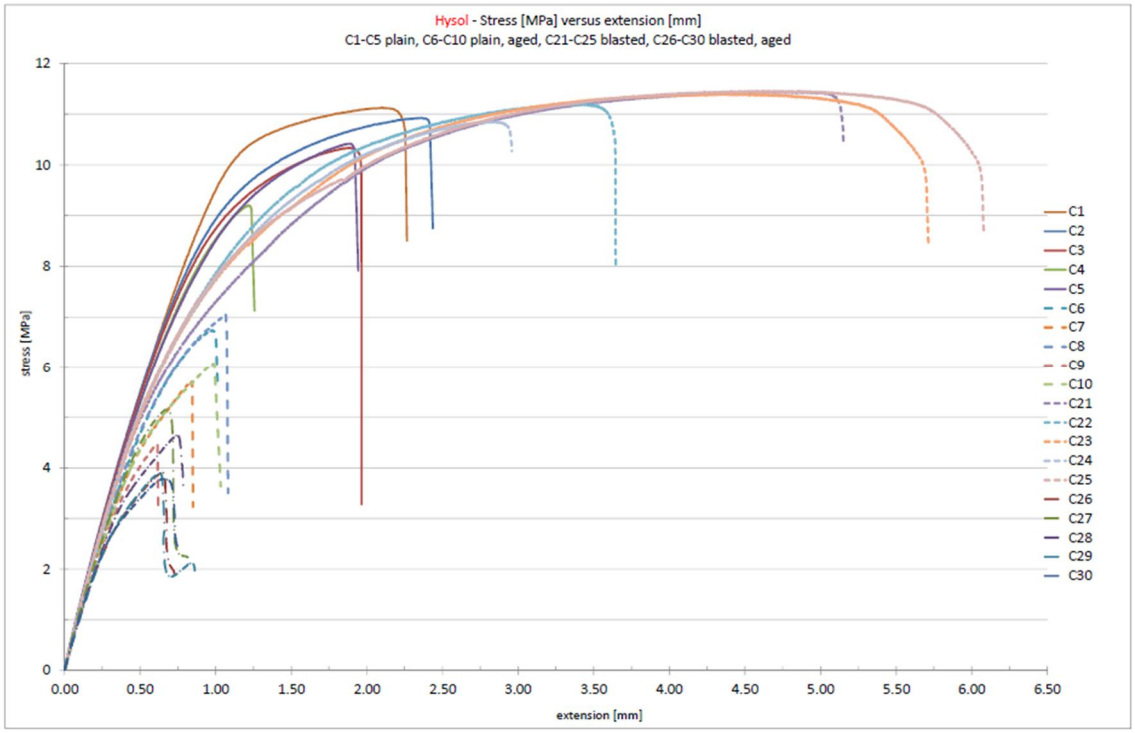

Figure 38 *Double strap shear stress curves of Hysol epoxy adhesive with thin plain (C1-10) and with thin glass blasted (C21-30) steel bond*

When compared the Hysol glass blasted steel specimen with and without hot water exposure (Figure 39) the dry thin and thick bond specimen gained the best results (yet deviation was larger with the thin bond). The specimen C35 was left out of the combined results as it clearly had some defect. Again the hot water exposure degraded the results; the thin and thick bonds had similar type of results, though the thick bond seemed more ductile.

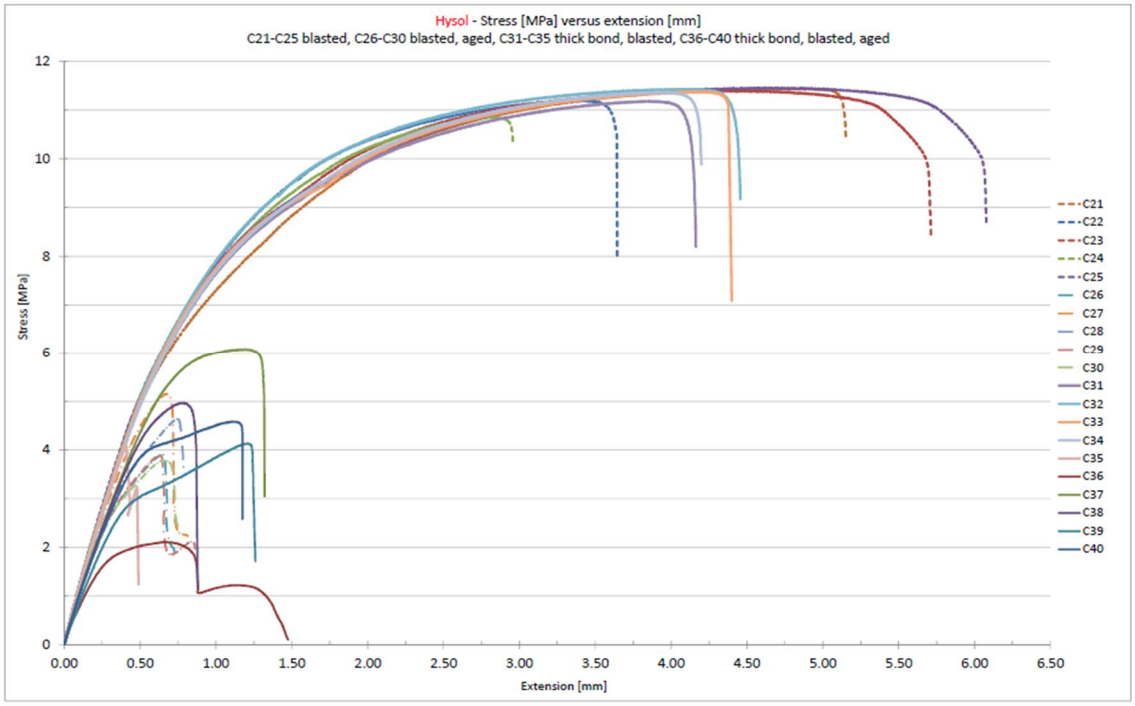

Figure 39 *Double strap shear stress curves of Hysol epoxy adhesive with thin (C21-30) and with thick (C31-40) glass blasted steel bond*

With Macroplast the results differ when compared to the other tested materials. The hot water exposure did not seem to affect much on the bond strength, though the glass blasting of the steel gained worse results when compared to the acetone wiped steel. The best, rather surprising, results (Figure 40) were with the hot water exposed acetone wiped steel specimen. No such strength increase could be seen with the glass blasted steel specimens. Because of the interesting results of the specimens D6-10 two extra specimens, DX1 and DX2, were prepared, post-cured one week at room temperature, aged for 9 hours at heat (80°C) only and double strap shear tested (Figure 41). Yet these results were more similar to the other than D6-10 results, though the slope of the stress-extension curve is gentler than with the others. Based on the previous an explanation for this rather unexpected result with D6-10 may be that the isocyanate had not properly reacted with polyol during curing. The composition with this unreacted isocyanate was then able to react with water during the hot water exposure. This reaction with water at the elevated temperature may have brought further urethane linkages or produced branching with the different end results such as isocyanurate or urea, amine or biuret groups instead of polyurethane. Those form also the network structures which may bond differently to the steel surface or have different properties.

The Instron 8801 testing equipment was used for the specimens D1-5 and D21-25 which may explain the steeper slope of these specimens compared to others.

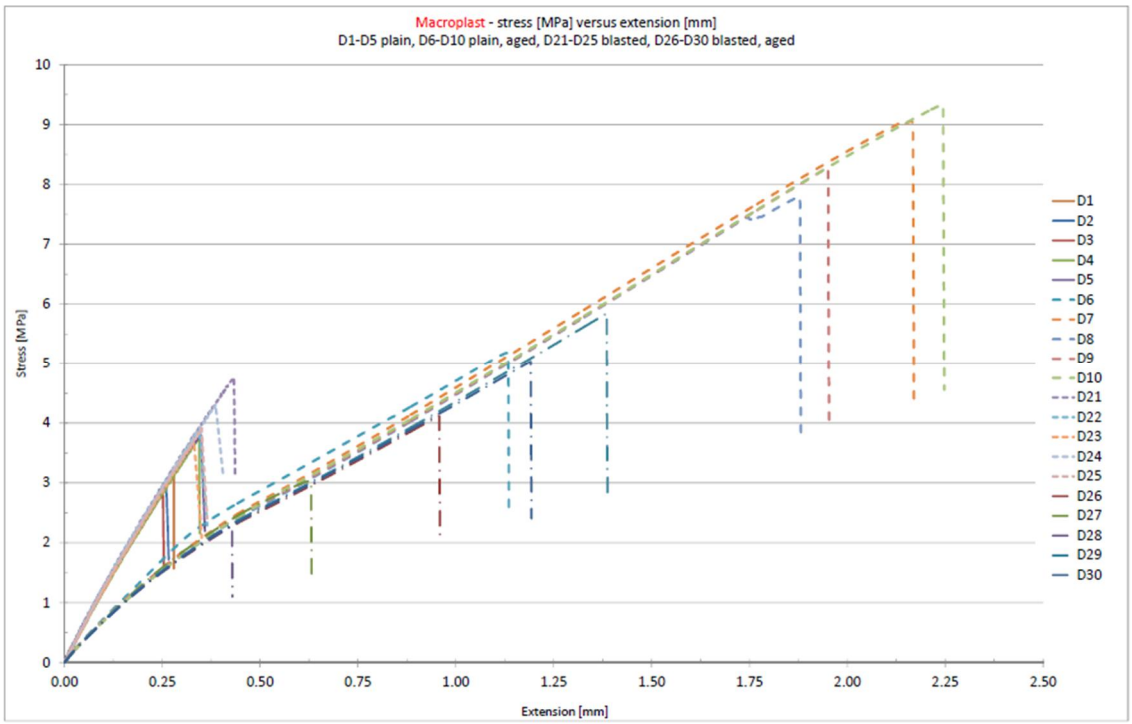

Figure 40 *Double strap shear stress curves of Macroplast polyurethane adhesive with thin plain (D1-10) and with thin glass blasted (D21-30) steel bond*

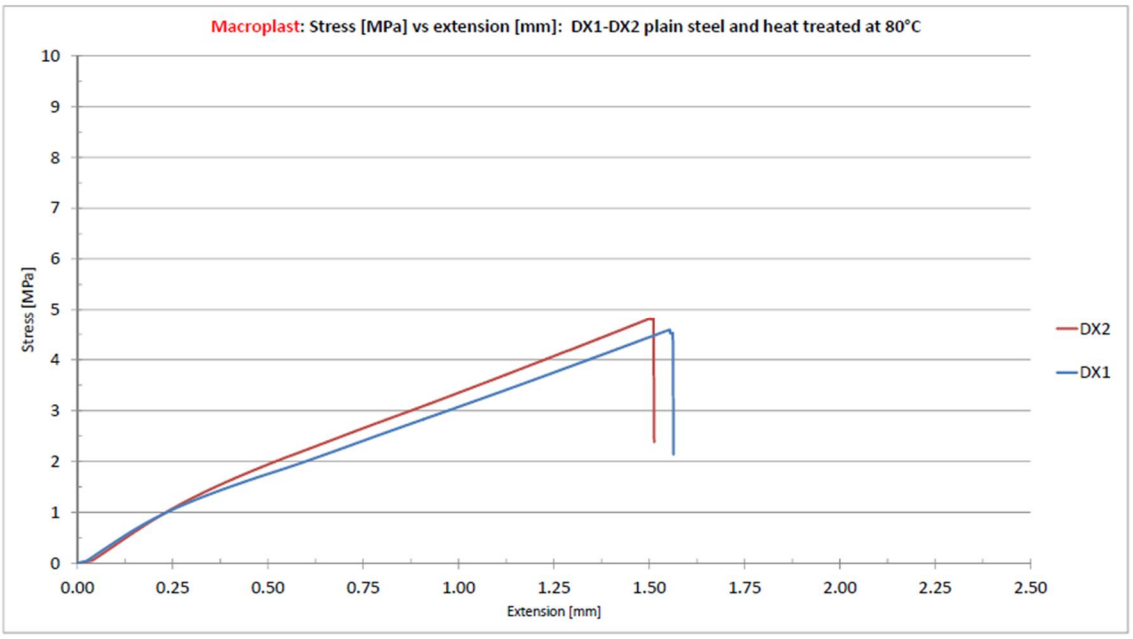

Figure 41 *Double strap shear stress curves of Macroplast polyurethane adhesive with heat treated (80°C) thin bond to acetone wiped steel (DX1-2)*

When compared the Macroplast glass blasted steel specimen with and without the hot water exposure (Figure 42) the results did not differ much; the dry thin bond specimen gained the best results. The Instron 8801 testing equipment was used for the

specimens D21-25 and D36-D40 which may explain the steeper slope of these specimens.

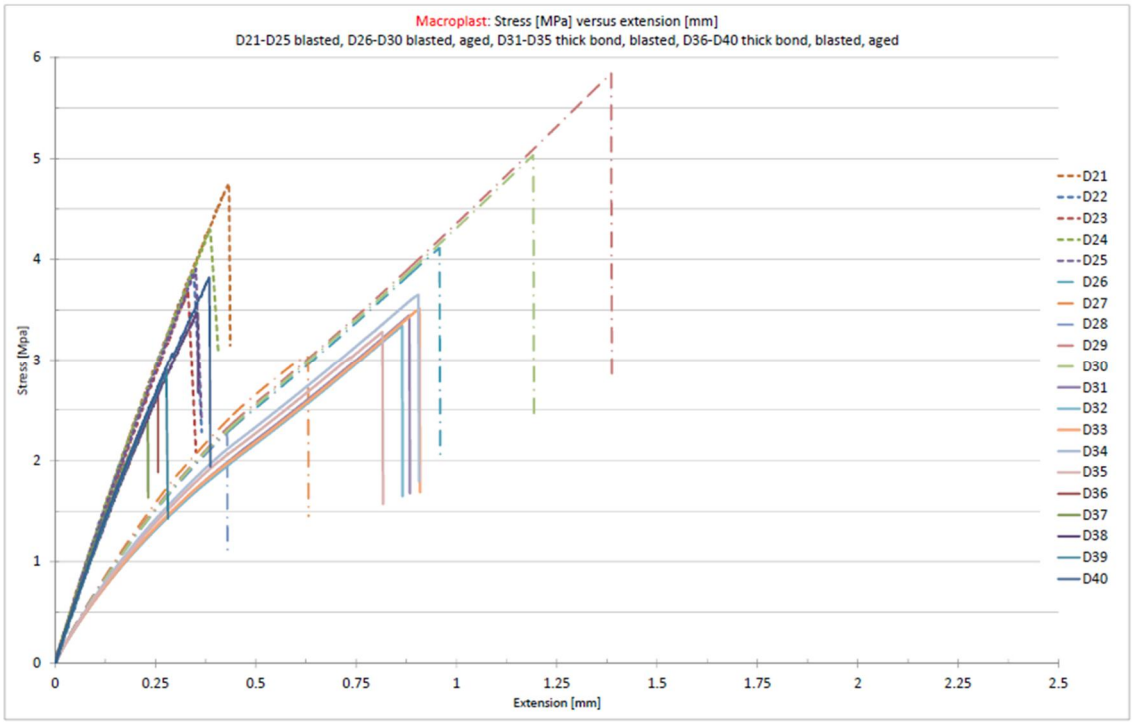

Figure 42 *Double strap shear stress curves of Macroplast polyurethane adhesive with thin (D21-30) and with thick (D31-40) glass blasted steel bond*

9.4 Bond strength

The maximum bond strengths were analysed from the test results. The strength was calculated by dividing the maximum load by the bond area:

$$\tau = \frac{F}{2*b*L} \quad , \tag{9.4}$$

where τ – shear strength, F – force, b – bond width, L – bond length.

The aqueous and hot environment seems to be hard on the properties of the studied materials as the strengths dropped drastically during only one week's exposure (Figure 43). The average drop was 38% (and 64% if the dissimilar Macroplast results are not counted). The exception to the poor results was the Macroplast polyurethane adhesive to which the hot water treatment did not affect much. Instead the strength got even better in hot water exposure with the acetone wiped specimens (D6-10).

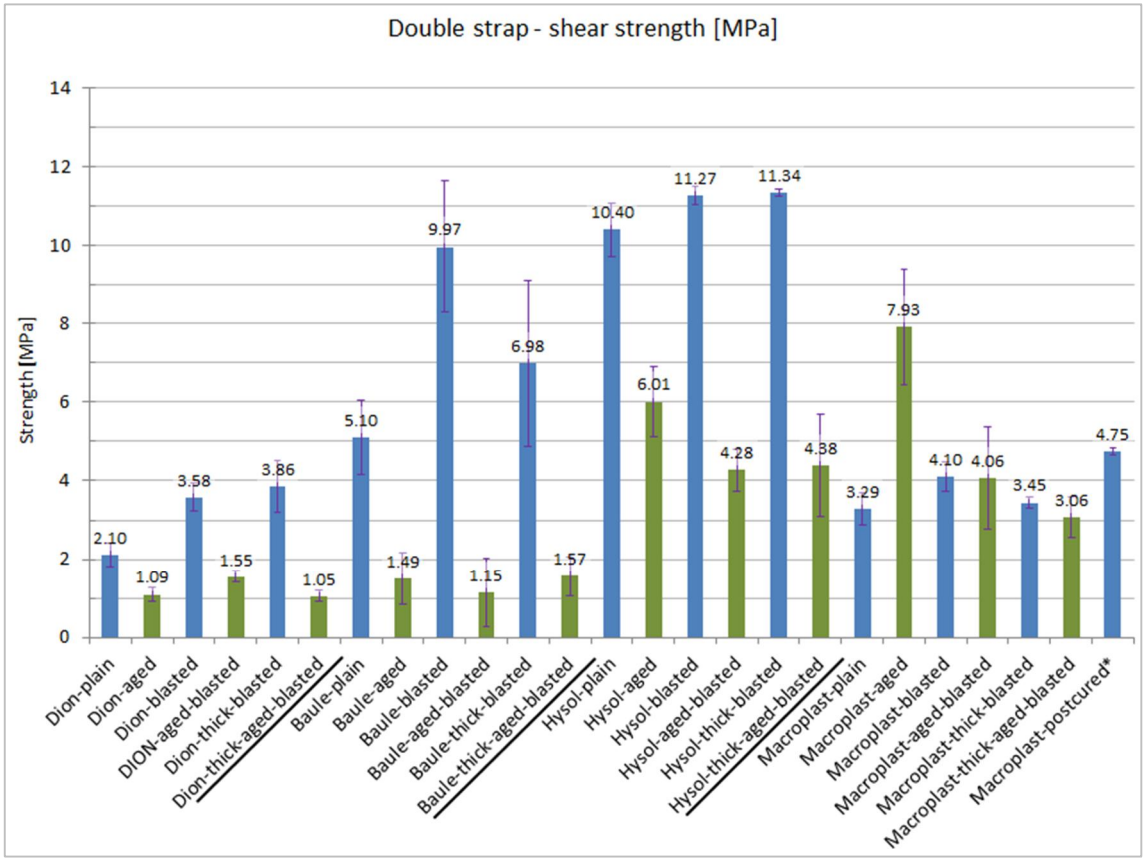

***Figure 43**: Double strap shear strength results of each specimen type*

When compared the acetone wiped plain steel with the glass blasted steel (Table 1) the results indicate that the glass blasting enhances the strength of the bond of all tested materials and both bond thicknesses at room temperature and normal RH. With Dion and Baule the increases were much higher than with Hysol and Macroplast, which probably may partly be explained with their lower viscosity values causing better steel surface pore penetration.

***Table 1** Plain steel bond strength changes caused by the glass blasting when compared to the acetone wiped steel in dry environment*

	Thin bond	Thick bond	Viscosity	
	strength change [%]	strength change [%]	min [Pa·s]	max [Pa·s]
Dion-vinyl ester resin	70%	84%	0.15	0.2
Baule-cast PU	95%	37%	1	2
Hysol-epoxy adhesive	8%	9%	15	60
Macroplast-PU adhesive	25%	5%	400	500

After the specimens were immersed in hot water the results show that the glass blasting actually does not help in hot and wet environment (Table 2). Though the glass blasting improved the resistance in the dry conditions the effectiveness diminished during the hot water exposure. One reason for the worse results with the glass blasted

specimen may be related to the viscosity of the material (yet the larger drops in overall strengths during the hot water exposure were gained with the more liquid materials). Thus to achieve a better/adequate adhesive penetration into the steel surface pores an extra pressure should likely be used with the more viscous materials during preparation and curing. Especially Macroplast has a high viscosity and also Hysol is thicker but still easily spreadable, whereas Baule has low and Dion very low viscosity. Moreover, most probably the moisture, which may have been absorbed by the polymer or diffused or travelled along the interface or via the pores, voids or cracks, is able to initiate the hydration of the steel surface oxides. Enhances to the bond strength with glass blasting in wet environment were gained with the Dion thin bond and the Baule thick bond only.

Table 2 *Strength of the hot water exposed glass blasted steel specimen compared to strength of the hot water exposed acetone wiped (plain) steel*

	Thin bond	Thick bond	Viscosity	
	strength change [%]	strength change [%]	min [Pa·s]	max [Pa·s]
Dion-vinyl ester resin	41%	-4%	0.15	0.2
Baule-cast PU	-23%	5%	1	2
Hysol-epoxy adhesive	-29%	-27%	15	60
Macroplast-PU adhesive	-49%	-61%	400	500

The retaining strengths after the hot water exposure (Figure 44) were calculated by comparing the maximum strength after the hot water treatment with the maximum strength without this treatment of each specimen type.

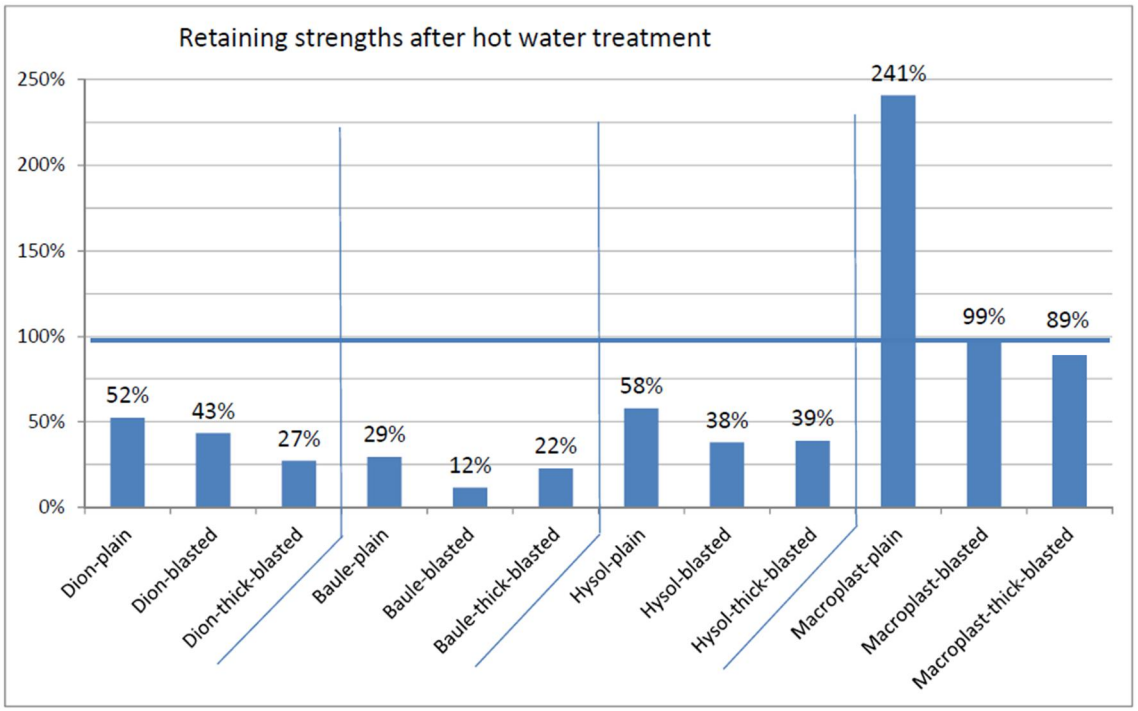

Figure 44 *Retaining strengths of each specimen type after hot water exposure*

As mentioned earlier Macroplast seems to retain its strength very well during the hot water exposure which was kind of surprise. Dion and Hysol behaved pretty much as was expected but the Baule behaviour was worse than expected (especially after the good Macroplast results the expectations for the cast polyurethane were good as well). Curing at 23°C may have had effect on the cast urethane behaviour as optimum curing temperature for the Baule's resin would have been 80-90°C (though curing at lower temperatures is possible when extended curing time is used).

9.5 Bond extension

Bond extension during the lap shear test was analysed from the test results at maximum load and at failure (Figure 45). In general with the vinyl ester resin (Dion) and polyurethane adhesive (Macroplast) the overall values are lower if compared to the cast polyurethane (Baule) and epoxy adhesive (Hysol). Dion and Macroplast show more brittle behaviour when visually and "manually" inspected. They also break immediately at maximum load as the extension values are same at maximum load and at failure.

So the higher extension values were gained with Baule and Hysol. The highest values are with a variable combination as follows: glass blasted steel, post curing at 23°C and normal RH for one week and thin bond line (though with Hysol thick bond line had high values too). To be noted that the specimen tested with Instron 8801 may result in the lower extension values compared to the specimen tested with Instron 5967. As due the heavier equipment (Instron 8801) the strain caused by the equipment itself may be smaller thus causing the lower results as well.

The strain values calculated from the bond extension at the maximum stress range from 0.19% to 8.42% (Table 3).

Table 3 *Specimen strains at maximum stress*

	Dion	Baule	Hysol	Macroplast	MIN	MAX
Plain steel - thin bond	0.41%	2.60%	3.78%	0.59%	0.41%	3.78%
Aged plain steel - thin bond	0.34%	1.83%	1.80%	3.75%	0.34%	3.75%
Glass blasted steel - thin bond	1.66%	8.42%	7.96%	0.74%	0.74%	8.42%
Aged glass blasted steel - thin bond	0.53%	1.41%	1.35%	1.84%	0.53%	1.84%
Glass blasted steel - thick bond	1.88%	5.03%	6.59%	1.75%	1.75%	6.59%
Aged glass blasted steel - thick bond	0.19%	3.48%	1.98%	0.60%	0.19%	3.48%

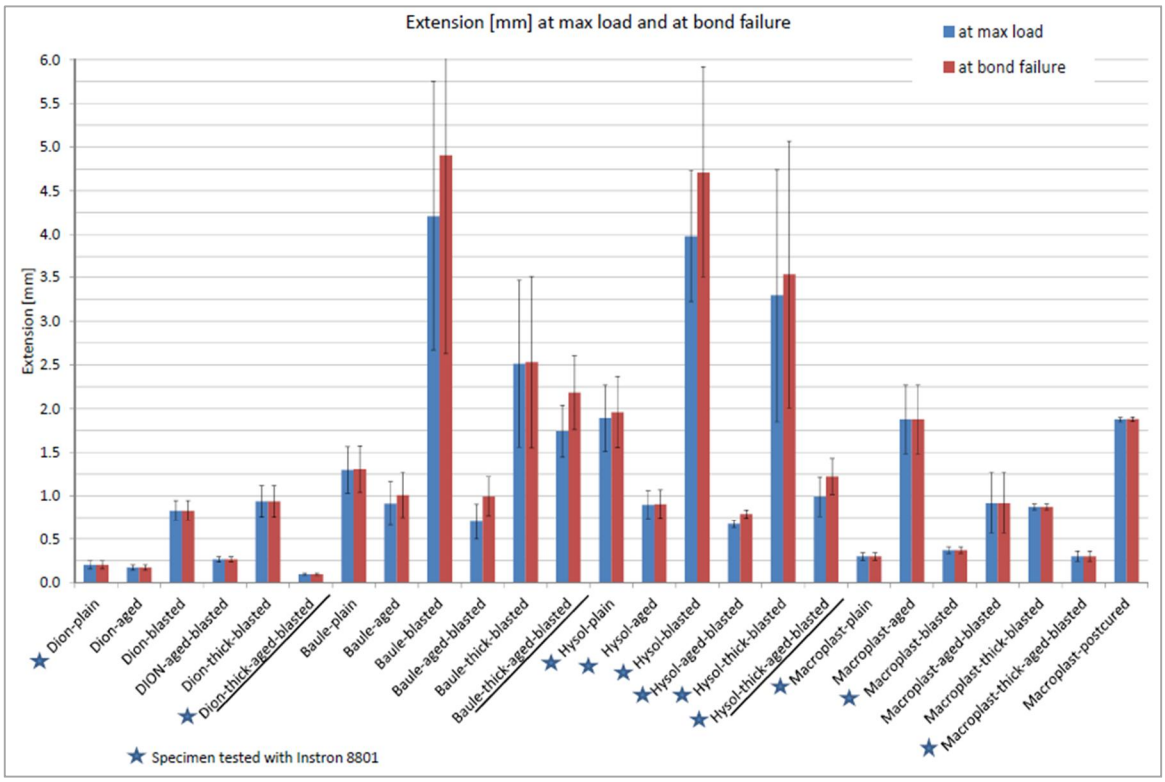

Figure 45 *Double strap bond extension results of each specimen type*

9.6 Failure mode

The specimen samples showed more and less different failure modes depending on the polymer, steel pre-treatment, bond thickness and water exposure. The figures 46-49 show an example of bond failure per each test variable combination.

The Dion specimen failure modes (Figure 46) were fully adhesive in all tests. Mostly with dry conditions (A1-5, A21-25, A31-35) the polymer broke partially across the bond, leaving material on both steel surfaces. Still the failure mode was adhesive as polymer was found only on one of the steel surfaces at that point. The polymer shows fracture at brittle manner if bent.

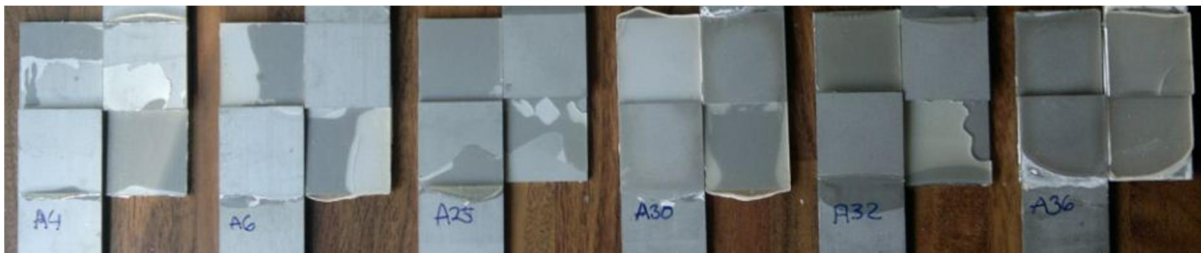

Figure 46 *Bond failures of the Dion specimens*

The Baule specimen failure modes (Figure 47) varied from adhesive to mixed mode. With the dry conditions and thin bond line (B1-5, B21-25) the polymer showed mixed

mode failure though the adhesive failure was dominant. With the hot water exposed thin bond on plain steel (B6-10) the polymer was found on the both steel surfaces but in that case the failure was adhesive.

The specimens were quite sticky right after the hot water exposure, but once cooled the effect disappeared. Additionally as a result of the gas formation (due the moisture absorption during preparation) the small bubbles could be seen in the polymer on the steel surface. Yet no bubbles (or much smaller size and lesser bubbles) were found inside the bond line. When bent the polymer is ductile and do not fracture easily.

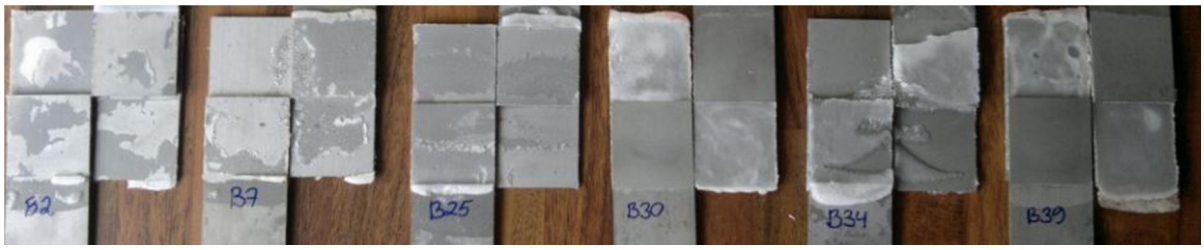

Figure 47 *Bond failures of the Baule specimens*

The Hysol specimen failure mode (Figure 48) was mainly adhesive, only slight signs of the cohesive (mixed) mode near the surface could be seen with dry conditions and thin bond line (C1-5, C21-25). With almost all specimens the polymer broke partially across the bond, but still at adhesive manner. The polymer seems quite ductile and do not fracture easily if bent.

Figure 48 *Bond failures of the Hysol specimens*

The Macroplast specimen failure modes (Figure 49) were adhesive and/or mixed. With the dry conditions and thin bond (D1-5, D21-25) and with all thick bond specimens (D31-40) the failure mode was adhesive. With the hot water exposed thin bond line specimens (D6-10, D26-30) the mode was mixed; on the areas in which the moisture absorbed the failure mode was adhesive, but the remaining area showed cohesive failure. Though this cohesive failure was still very near the adhesive surface (Figure 50) thus most probably the failure was caused by a degradation of the interface (as upon moisture penetration the locus of failure almost always is at or near the interface, and the metal oxide surfaces attract water molecules causing disruption of the

dispersive bonds of the interface [27]). The heat exposed extra specimen (DX1-2) showed adhesive failure mode, though slight signs of cohesive failure very near the polymer surface existed. When bent the polymer fractures at brittle manner.

Figure 49 *Bond failures of the Macroplast specimens*

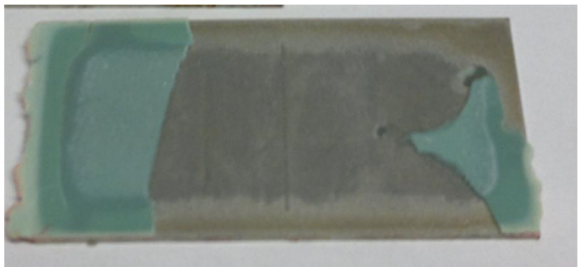

Figure 50 *Detail about the Macroplast mixed mode failure*

10 CONCLUSIONS

The adequate static shear strength of the joint with the ambient testing environment does not necessarily translate to a good performance under the operating environment. This was also shown during this thesis work. The overall strength results of the tested materials were somewhat below that was expected. With some of the materials even the initial strengths before the hot water exposure were already quite low compared to the results would be expected based on the technical data sheets. Anyway, the different results (yet almost all bonds failed adhesively) were achieved depending on the used double-lap-shear test variables (polymer material, pre-treatment method, adhesive bond thickness and ageing), still none of the materials was superior to the others. The combination of load, elevated temperature and humidity caused very rapid loss of the joint strength. It was also observed that with the cast polyurethane special care is needed during mixing and preparation as it quickly and easily reacts with the ambient moisture.

The glass blasting of the steel surface enhanced the bond strength in dry environment, but according to the test results it may not be the most appropriate or effective enough pre-treatment option for the hot and wet environment, at least if used alone. As the blasting produces a rougher surface it may be more difficult to the adhesive to penetrate into the surface pores (and even more difficult if the viscosity of the penetrating material is high). In addition as the viscosity in the adhesive often increases rapidly the adhesive may not have enough time to reach all pores thus leaving voids at the interface. All in all, blasting seems to offer water a way to penetrate into the interface more easily. As a result the hydrated steel oxides give rise to the bond failure as the chemical bonds are displaced. Therefore the more effective pre-treatment methods or usage of a steel coating or primer, which preserve the treated surface and provides resistance to hydrolysis, should be analysed and tested. For example the suitability of the silane treatment or sol-gel coating for the steel surface could be studied. Also plasma treatment may be an effective method, besides it has a low environmental impact.

As curing of the materials was done at room temperature some post-curing may have happened during the ageing period which may influence the results. Additionally curing

at elevated temperature usually raises the polymer's T_g, and also curing itself may reach the fully completed state easier in a warmer environment. So curing/post-curing at higher temperature could be tested, at least with Baule, which results may have declined more because of the room temperature cure.

In general there are several ways to enhance the bonded joint performance within the hybrid structure. The following methods came up during this thesis work. The perforation of the steel blades may enhance the adhesion between the polymer and steel or the strength of the whole structure as the blades are then stronger attached to the component structure. Also placing some rod or pole perpendicular through the steel blades and inside the polymer may strengthen the structure. The shape of the mould may also effect on the durability; for example by using the fillet profile for the polymer around the steel blades the joint durability may be enhanced. By adding certain type of fillers to the adhesive/polymer may lead to enhanced durability towards water. And if the matching metallic fillers are used the polymer's CTE can be lowered (if needed at all, as the effect of thermal expansion was not studied in this thesis work).

As the loads and therefore the stresses in the currently used cast steel component (and thus the strength requirements for the hybrid component either) are not known well at least some of the tested materials (likely the Hysol and Macroplast adhesives) may well be strong enough to form a proper hybrid structure. Still the additional materials should be analysed and tested in order to find a better performing option compared to these which were used and researched in this thesis work. For example, some epoxy resin or the other cast polyurethane, polyurethane adhesive or epoxy adhesive with the different composition or chemistry could be tested. As a suggestion, cast polyurethane might be worth further testing as with it there seems to be several options to tailor the properties to match the application needs and the application areas for the polyurethanes are invariably expanded. Anyhow it is important to find a polymer material with a good adhesion to the stainless steel and which do not absorb moisture easily and thus ease hydration of the polymer-steel interface.

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APPENDIX 1: POLYMER MATERIAL PROPERTIES

Reichhold: Dion 9102

- 2-K bisphenol-epoxy vinyl ester resin
- Viscosity at 23°C: 150-200 mPa·s
- Pot life: 25-30 min, setting time: 2 hours
- Curing at room temperature
- Notes: very low viscosity, yet possible to obtain the desired bond thicknesses. Once hardened seems brittle

Baule: CG9 9086 82D MF Polyol + B9 M10 MF Iso

- 2-K cast polyurethane (MDI-Ether based system)
- Viscosity at 23°C: 1-2 Pa·s
- Pot life: 15 min (or less), setting time: 1-2 hour
- Processing at room temperature, curing temperature recommended at 80(-90)°C (requires longer curing time if lower temperature used)
- Price: 2 kg 19,59€
- Notes: once opened the isocyanate component containers must be closed under dry inert gas (for example nitrogen may be used), mixed material may foam quite easily. Once hardened seems tough/ductile

Henkel: Hysol 9466

- Toughened 2K-epoxy adhesive, bisphenol-A epichlorhydrin resin, hardener oxybis (ethyleneepoxy)bis(propylamine)
- Operating temperature max 120°C
- Viscosity at 23°C: 15-60 Pa·s
- Pot life: 60 min, setting time: around 8 hours
- Curing at room temperature
- Price: 400ml 55,56€
- Notes: not exactly liquid but a bit thicker, still spreads easily. Once hardened seems tough/ductile. Setting at room temperature took long time

Henkel: Macroplast 1351 B25

- Solvent-free 2K-polyurethane adhesive, polypropylene glycol, hardener diphenyl methane-(di)isocyanate
- Operating temperature max 120°C
- Viscosity at 20°C: 400-500 Pa·s
- Pot life: 20 min, setting time: 1-2 hours
- Curing at 15-80°C
- Price: 400 ml 71,71€
- Notes: like toothpaste, still spreadable but after 15 min texture started to be more like chewing gum. Once hardened seems brittle

APPENDIX 2: TESTING RELATED STANDARDS

Test number	Test title	Test area/topic
ASTM D256	Standard Test Methods for Determining the Izod Pendulum Impact Resistance of Plastics	impact
ASTM D638	Standard Test Method for Tensile Properties of Plastics	tension
ASTM D648	Standard Test Method for Deflection Temperature of Plastics Under Flexural Load in the Edgewise Position	temperature
ASTM D671	Standard Test Method for Flexural Fatigue of Plastics by Constant-Amplitude-of-Force	fatigue
ASTM D950	Standard Test Method for Impact Strength of Adhesive Bonds	impact
ASTM D1002	Standard Test Method for Apparent Shear Strength of Single-Lap-Joint Adhesively Bonded Metal Specimens by Tension Loading	shear
ASTM D1044	Standard Test Method for Resistance of Transparent Plastics to Surface Abrasion	wear
ASTM D1781-76	Standard Test Method for Climbing Drum Peel for Adhesives	peel
ASTM D1876	Standard Test Method for Peel Resistance of Adhesives (T-Peel Test)	peel
ASTM D2990	Standard Test Methods for Tensile, Compressive, and Flexural Creep and Creep-Rupture of Plastics	creep
ASTM D3166	Standard Test Method for Fatigue Properties of Adhesives in Shear by Tension Loading (Metal/Metal)	fatigue
ASTM D3167	Standard Test Method for Floating Roller Peel Resistance of Adhesives	peel
ASTM D3433	Standard Test Method for Fracture Strength in Cleavage of Adhesives in Bonded Metal Joints	wedge
ASTM D3528	Standard Test Method for Strength Properties of Double Lap Shear Adhesive Joints by Tension Loading	shear
ASTM D3762	Standard Test Method for Adhesive-Bonded Surface Durability of Aluminum (Wedge Test)	wedge
ASTM D4065-06	Standard Practice for Plastics: Dynamic Mechanical Properties: Determination and Report of Procedures	dynamic
ASTM D5420	Standard Test Method for Impact Resistance of Flat, Rigid Plastic Specimen by Means of a Striker Impacted by a Falling Weight (Gardner Impact)	impact
ASTM D5628	Standard Test Method for Impact Resistance of Flat, Rigid Plastic Specimens by Means of a Falling Dart (Tup or Falling Mass)	impact
ASTM D5656	Standard Test Method for Thick-Adherend Metal Lap-Shear Joints for Determination of the Stress-Strain Behavior of Adhesives in Shear by Tension Loading	shear
ASTM D7136	Standard Test Method for Measuring the Damage Resistance of a Fiber-Reinforced Polymer Matrix Composite to a Drop-Weight Impact Event	compression
ASTM D7137	Standard Test Method for Compressive Residual Strength Properties of Damaged Polymer Matrix Composite Plates	compression
ASTM E2092-09	Standard Test Method for Distortion Temperature in Three-Point Bending by Thermomechanical Analysis	temperature
ASTM G77	Standard Test Method for Ranking Resistance of Materials to Sliding Wear Using Block-on-Ring Wear Test	wear
ASTM G99	Standard Test Method for Wear Testing with a Pin-on-Disk Apparatus	wear
ASTM G176	Standard Test Method for Ranking Resistance of Plastics to Sliding Wear using Block-on-Ring Wear Test—Cumulative Wear Method	wear
DIN 53462:1987-01	Testing of plastics; martens method of determining the temperature of deflection under abending stress	temperature
DIN EN 1465:2009	Adhesives - Determination of tensile lap-shear strength of bonded assemblies	shear
DIN EN ISO 604:2003-12	Plastics - Determination of compressive properties	compression
ISO 179	Determination of Charpy impact properties	impact
ISO 180	Determination of Izod impact strength	impact
ISO 306	Determination of Vicat softening temperature (VST)	temperature
ISO 527	Determination of tensile properties	tension
ISO 899	Determination of creep behaviour	creep
ISO 4587	Determination of tensile lap-shear strength of rigid-to-rigid bonded assemblies	shear
ISO 6721-2:2008	Plastics - Determination of dynamic mechanical properties - Part 2: Torsion-pendulum method	dynamic
ISO 8510-2	Peel test for a flexible-bonded-to-rigid test specimen assembly	peel
ISO 9352	Determination of resistance to wear by abrasive wheels	wear
ISO 9653	Test method for shear impact strength of adhesive bonds	impact
ISO 9664	Test methods for fatigue properties of structural adhesives in tensile shear	fatigue
ISO 10354	Characterization of durability of structural-adhesive-bonded assemblies -- Wedge rupture test	wedge
ISO 11003-2	Determination of shear behaviour of structural adhesives	shear
ISO 11339	T-Peel Test Flexible to Flexible Bonded Assemblies	peel
ISO 11343	Adhesives -- Determination of dynamic resistance to cleavage of high-strength adhesive bonds under impact conditions -- Wedge impact method	wedge
ISO 15024:2001	Fibre-reinforced plastic composites -- Determination of mode I interlaminar fracture toughness, GIC, for unidirectionally reinforced materials	wedge
ISO 15108: 1998	Adhesives–Determination of strength of bonded joints using a bending–shear method	wedge

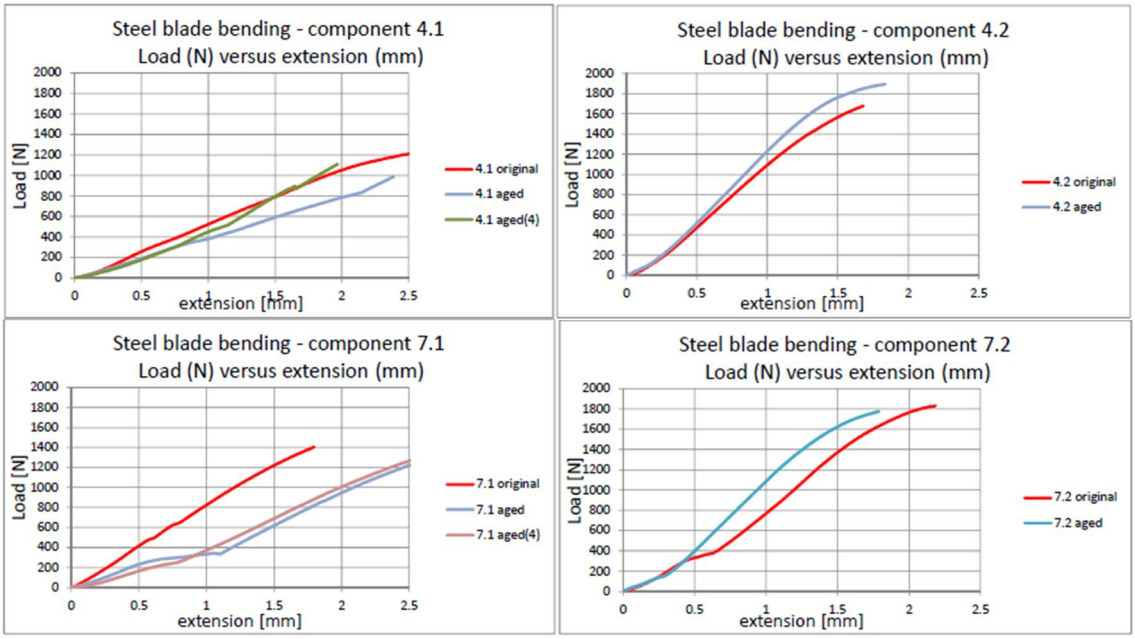
APPENDIX 3: MEASUREMENT MATRIX

THIN BOND			THIN BOND			THICK BOND		
Reichhold - Dion						Reichhold - Dion		
-ageing 1: 23°C, 7 days	A1	-pre-treatment 1: acetone	-ageing 1	A21	-pre-treatment 2	-ageing 1	A31	-pre-treatment 2
-ageing 1: 23°C, 7 days	A2	-pre-treatment 1: acetone	-ageing 1	A22	-pre-treatment 2	-ageing 1	A32	-pre-treatment 2
-ageing 1: 23°C, 7 days	A3	-pre-treatment 1: acetone	-ageing 1	A23	-pre-treatment 2	-ageing 1	A33	-pre-treatment 2
-ageing 1: 23°C, 7 days	A4	-pre-treatment 1: acetone	-ageing 1	A24	-pre-treatment 2	-ageing 1	A34	-pre-treatment 2
-ageing 1: 23°C, 7 days	A5	-pre-treatment 1: acetone	-ageing 1	A25	-pre-treatment 2	-ageing 1	A35	-pre-treatment 2
THIN BOND			THIN BOND			THICK BOND		
Reichhold - Dion						Reichhold - Dion		
-ageing 2: 80°C water, 7 days	A6	-pre-treatment 1: acetone	-ageing 2	A26	-pre-treatment 2	-ageing 2	A36	-pre-treatment 2
-ageing 2: 80°C water, 7 days	A7	-pre-treatment 1: acetone	-ageing 2	A27	-pre-treatment 2	-ageing 2	A37	-pre-treatment 2
-ageing 2: 80°C water, 7 days	A8	-pre-treatment 1: acetone	-ageing 2	A28	-pre-treatment 2	-ageing 2	A38	-pre-treatment 2
-ageing 2: 80°C water, 7 days	A9	-pre-treatment 1: acetone	-ageing 2	A29	-pre-treatment 2	-ageing 2	A39	-pre-treatment 2
-ageing 2: 80°C water, 7 days	A10	-pre-treatment 1: acetone	-ageing 2	A30	-pre-treatment 2	-ageing 2	A40	-pre-treatment 2
THIN BOND			THIN BOND			THICK BOND		
Baule - cast PU			Baule - cast PU			Baule - cast PU		
-ageing 1: 23°C, 7 days	B1	-pre-treatment 1: acetone	-ageing 1	B21	-pre-treatment 2	-ageing 1	B31	-pre-treatment 2
-ageing 1: 23°C, 7 days	B2	-pre-treatment 1: acetone	-ageing 1	B22	-pre-treatment 2	-ageing 1	B32	-pre-treatment 2
-ageing 1: 23°C, 7 days	B3	-pre-treatment 1: acetone	-ageing 1	B23	-pre-treatment 2	-ageing 1	B33	-pre-treatment 2
-ageing 1: 23°C, 7 days	B4	-pre-treatment 1: acetone	-ageing 1	B24	-pre-treatment 2	-ageing 1	B34	-pre-treatment 2
-ageing 1: 23°C, 7 days	B5	-pre-treatment 1: acetone	-ageing 1	B25	-pre-treatment 2	-ageing 1	B35	-pre-treatment 2
THIN BOND			THIN BOND			THICK BOND		
Baule - cast PU			Baule - cast PU			Baule - cast PU		
-ageing 2: 80°C water, 7 days	B6	-pre-treatment 1: acetone	-ageing 2	B26	-pre-treatment 2	-ageing 2	B36	-pre-treatment 2
-ageing 2: 80°C water, 7 days	B7	-pre-treatment 1: acetone	-ageing 2	B27	-pre-treatment 2	-ageing 2	B37	-pre-treatment 2
-ageing 2: 80°C water, 7 days	B8	-pre-treatment 1: acetone	-ageing 2	B28	-pre-treatment 2	-ageing 2	B38	-pre-treatment 2
-ageing 2: 80°C water, 7 days	B9	-pre-treatment 1: acetone	-ageing 2	B29	-pre-treatment 2	-ageing 2	B39	-pre-treatment 2
-ageing 2: 80°C water, 7 days	B10	-pre-treatment 1: acetone	-ageing 2	B30	-pre-treatment 2	-ageing 2	B40	-pre-treatment 2
THIN BOND			THIN BOND			THICK BOND		
Henkel - Hysol 9466			Henkel - Hysol 9466			Henkel - Hysol 9466		
-ageing 1: 23°C, 7 days	C1	-pre-treatment 1: acetone	-ageing 1	C21	-pre-treatment 2	-ageing 1	C31	-pre-treatment 2
-ageing 1: 23°C, 7 days	C2	-pre-treatment 1: acetone	-ageing 1	C22	-pre-treatment 2	-ageing 1	C32	-pre-treatment 2
-ageing 1: 23°C, 7 days	C3	-pre-treatment 1: acetone	-ageing 1	C23	-pre-treatment 2	-ageing 1	C33	-pre-treatment 2
-ageing 1: 23°C, 7 days	C4	-pre-treatment 1: acetone	-ageing 1	C24	-pre-treatment 2	-ageing 1	C34	-pre-treatment 2
-ageing 1: 23°C, 7 days	C5	-pre-treatment 1: acetone	-ageing 1	C25	-pre-treatment 2	-ageing 1	C35	-pre-treatment 2
THIN BOND			THIN BOND			THICK BOND		
Henkel - Hysol 9466			Henkel - Hysol 9466			Henkel - Hysol 9466		
-ageing 2: 80°C water, 7 days	C6	-pre-treatment 1: acetone	-ageing 2	C26	-pre-treatment 2	-ageing 2	C36	-pre-treatment 2
-ageing 2: 80°C water, 7 days	C7	-pre-treatment 1: acetone	-ageing 2	C27	-pre-treatment 2	-ageing 2	C37	-pre-treatment 2
-ageing 2: 80°C water, 7 days	C8	-pre-treatment 1: acetone	-ageing 2	C28	-pre-treatment 2	-ageing 2	C38	-pre-treatment 2
-ageing 2: 80°C water, 7 days	C9	-pre-treatment 1: acetone	-ageing 2	C29	-pre-treatment 2	-ageing 2	C39	-pre-treatment 2
-ageing 2: 80°C water, 7 days	C10	-pre-treatment 1: acetone	-ageing 2	C30	-pre-treatment 2	-ageing 2	C40	-pre-treatment 2
THIN BOND			THIN BOND			THICK BOND		
Henkel - Macroplast 1351			Henkel - Macroplast 1351			Henkel - Macroplast 1351		
-ageing 1: 23°C, 7 days	D1	-pre-treatment 1: acetone	-ageing 1	D21	-pre-treatment 2	-ageing 1	D31	-pre-treatment 2
-ageing 1: 23°C, 7 days	D2	-pre-treatment 1: acetone	-ageing 1	D22	-pre-treatment 2	-ageing 1	D32	-pre-treatment 2
-ageing 1: 23°C, 7 days	D3	-pre-treatment 1: acetone	-ageing 1	D23	-pre-treatment 2	-ageing 1	D33	-pre-treatment 2
-ageing 1: 23°C, 7 days	D4	-pre-treatment 1: acetone	-ageing 1	D24	-pre-treatment 2	-ageing 1	D34	-pre-treatment 2
-ageing 1: 23°C, 7 days	D5	-pre-treatment 1: acetone	-ageing 1	D25	-pre-treatment 2	-ageing 1	D35	-pre-treatment 2
THIN BOND			THIN BOND			THICK BOND		
Henkel - Macroplast 1351			Henkel - Macroplast 1351			Henkel - Macroplast 1351		
-ageing 2: 80°C water, 7 days	D6	-pre-treatment 1: acetone	-ageing 2	D26	-pre-treatment 2	-ageing 2	D36	-pre-treatment 2
-ageing 2: 80°C water, 7 days	D7	-pre-treatment 1: acetone	-ageing 2	D27	-pre-treatment 2	-ageing 2	D37	-pre-treatment 2
-ageing 2: 80°C water, 7 days	D8	-pre-treatment 1: acetone	-ageing 2	D28	-pre-treatment 2	-ageing 2	D38	-pre-treatment 2
-ageing 2: 80°C water, 7 days	D9	-pre-treatment 1: acetone	-ageing 2	D29	-pre-treatment 2	-ageing 2	D39	-pre-treatment 2
-ageing 2: 80°C water, 7 days	D10	-pre-treatment 1: acetone	-ageing 2	D30	-pre-treatment 2	-ageing 2	D40	-pre-treatment 2

EXTRAS		
THIN BOND		
Henkel - Macroplast 1351		
-ageing: 80°C, 7 days	Dx1	-pre-treatment 1: acetone
-ageing: 80°C, 7 days	Dx2	-pre-treatment 1: acetone

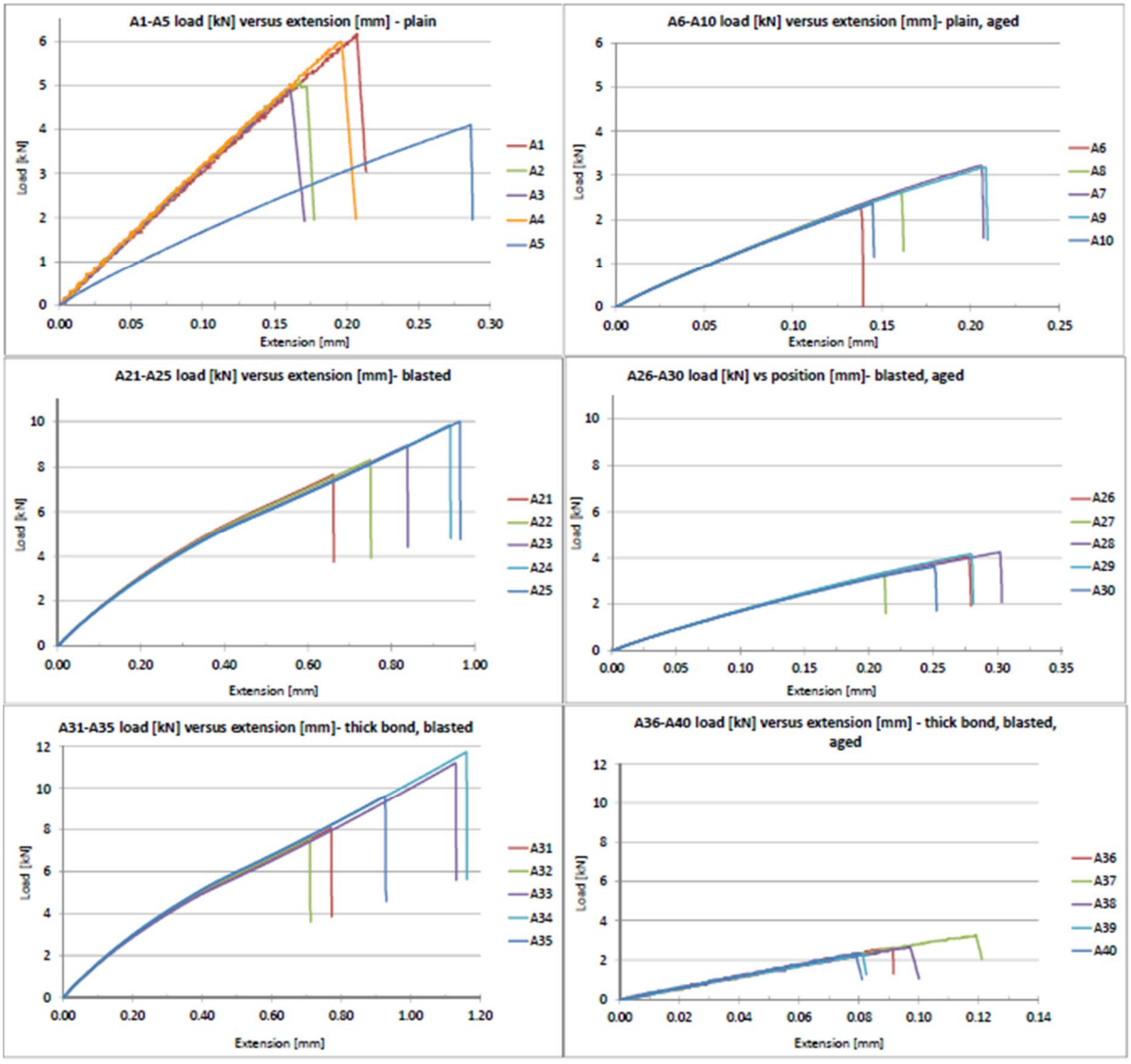
APPENDIX 4: TEST RESULTS – HYBRID COMPONENT: LOAD VERSUS EXTENSION

Derakane vinyl ester resin was used for the test specimen 4.1-4.2 and Dion vinyl ester resin for the specimen 7.1-7.2. Specimen 4.1 and 7.1 have plain polymer between the steel blades. Specimens 4.2 and 7.2 have steel inserts between the steel blades.



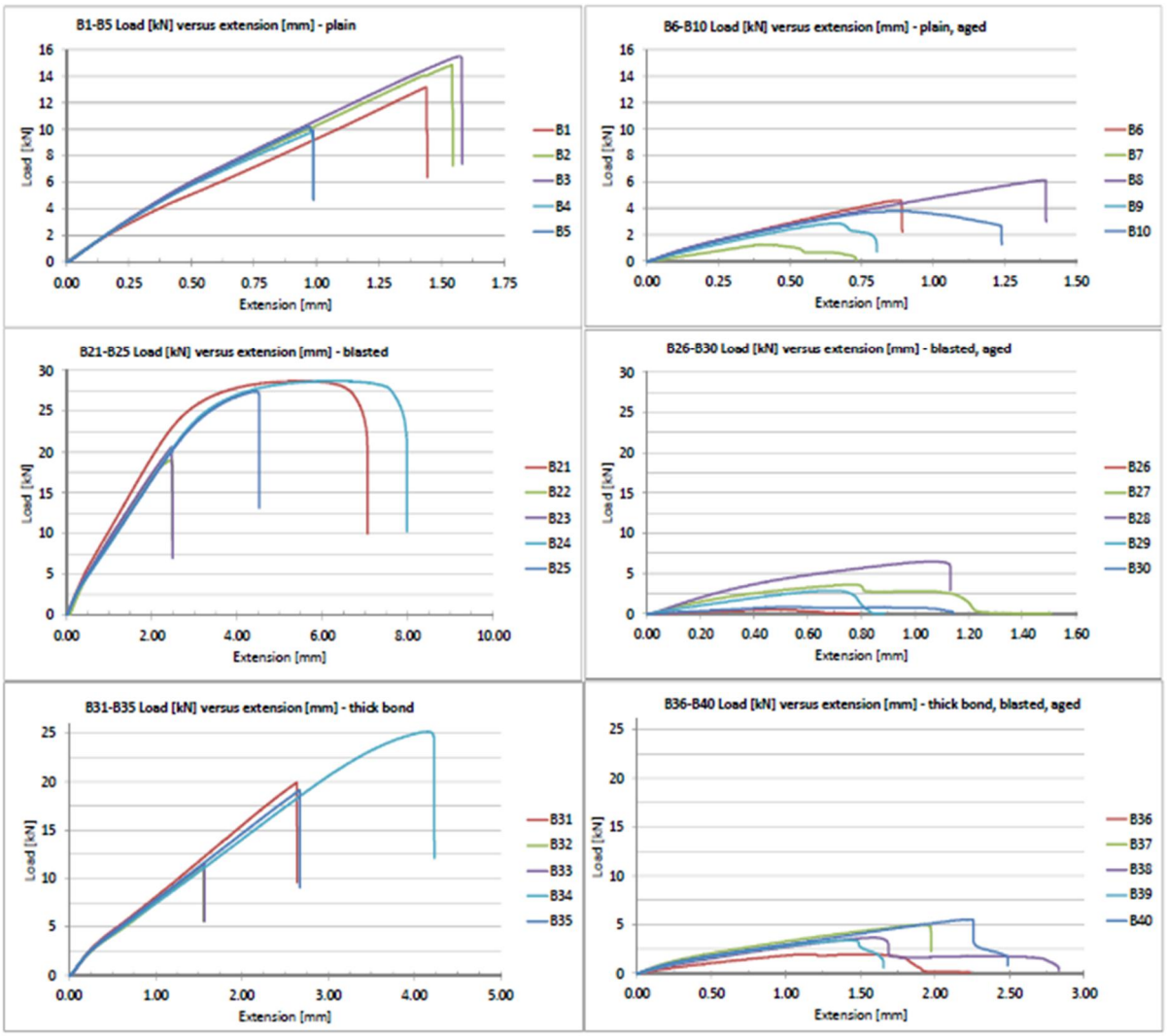
APPENDIX 5: TEST RESULTS – DOUBLE STRAP BOND: LOAD VERSUS EXTENSION

Dion vinyl ester resin was used for the test specimens A1-A5, A6-A10, A21-A25, A26-A30, A31-A35, A36-A40. The double-strap shear test results - Load (kN) versus extension (mm):

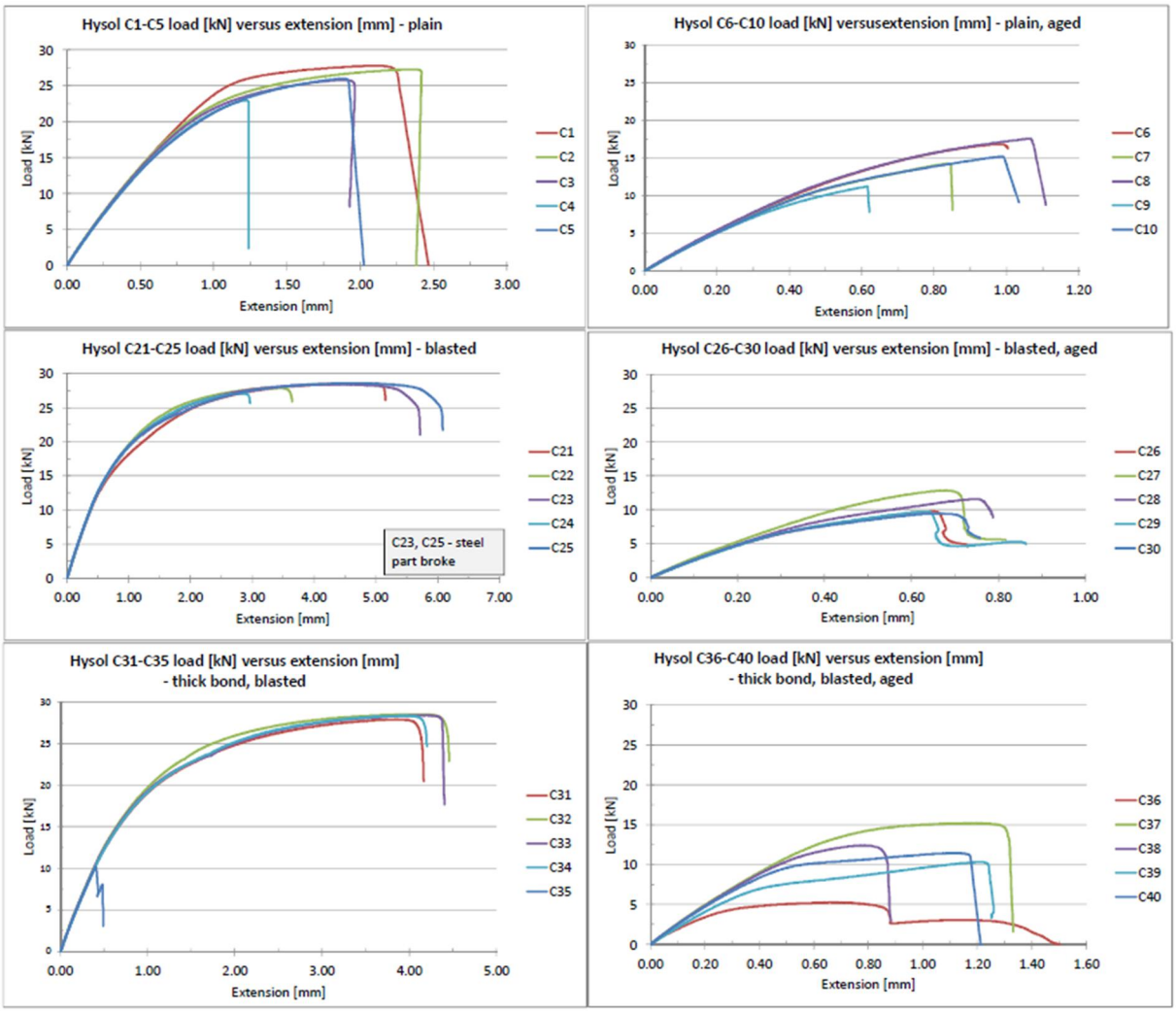


Baule cast polyurethane resin was used for the test specimens B1-B5, B6-B10, B21-B25, B26-B30, B31-B35, B36-B40.

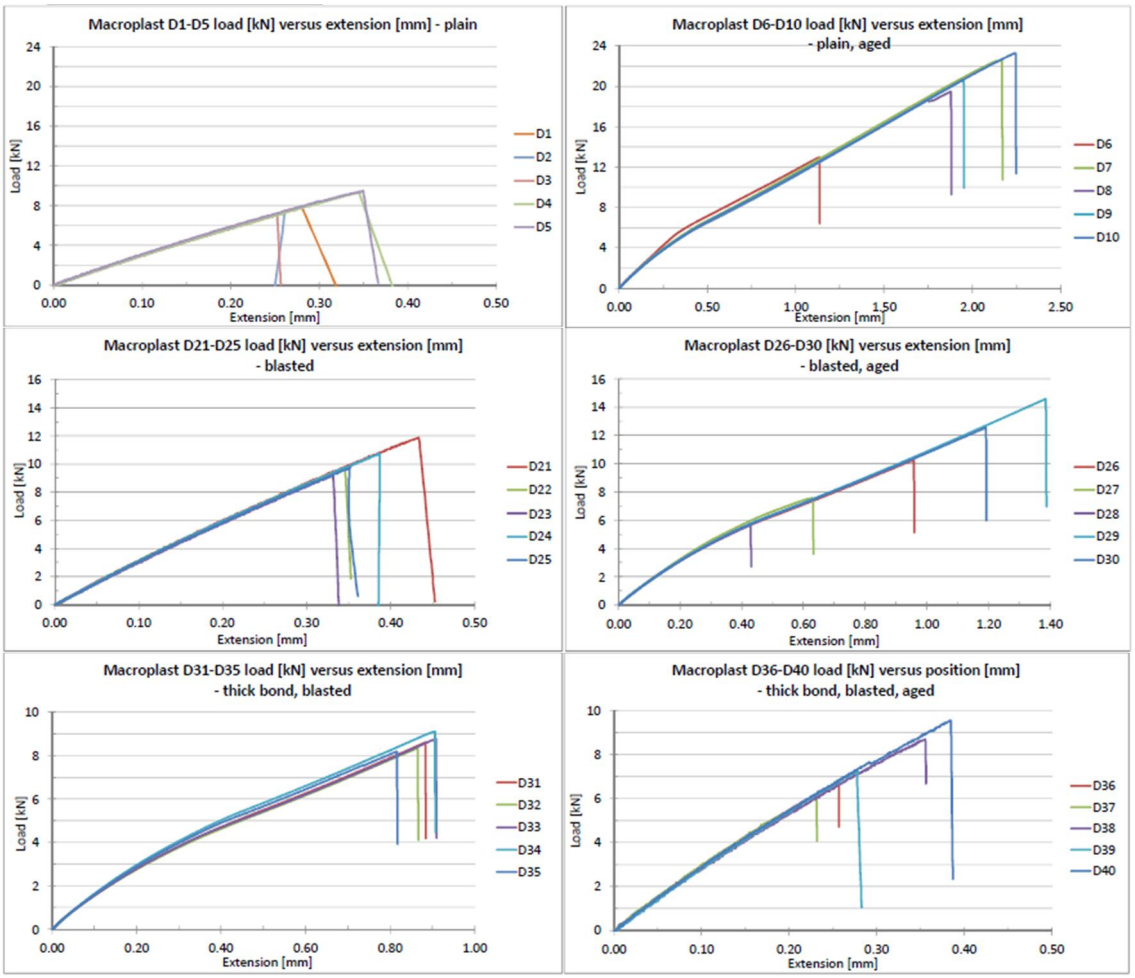
The double-strap shear test results - Load (kN) versus extension (mm):



Hysol epoxy adhesive was used for the test specimens C1-C5, C6-C10, C21-C25, C26-C30, C31-C35, C36-C40. The double-strap shear test results - Load (kN) versus extension (mm):



Macroplast polyurethane adhesive was used for the test specimens D1-D5, D6-D10, D21-D25, D26-D30, D31-D35, D36-D40. The double-strap shear test results - Load (kN) versus extension (mm):



Two extra Macroplast specimens, DX1 and DX2, were prepared with postcuring in heat (80°C) for 10 hours. The double-strap shear test results - Load (kN) versus extension (mm):